April, 1934

RUBBER CHEMISTRY AND TECHNOLOGY

Published under the Auspices of the
RUBBER DIVISION *of the* AMERICAN CHEMICAL SOCIETY

VOLUME VII NUMBER 2

MICRONEX

The Master Colloid

Built from the atoms of Millions of Flames.

Ensures the durability of your products by application of the King of Colloidal Carbons to your rubber compounds.

BINNEY & SMITH CO.

Specialists in CARBON BLACKS, STEARIC ACID, IRON OXIDES, MINERAL RUBBER and other products for the rubber industry.

41 East 42nd St., New York, N. Y.

The Magic Lamp, Your Protection for Over 50 Years

RUBBER CHEMISTRY AND TECHNOLOGY

Published quarterly under the Auspices of the Rubber Division
of the American Chemical Society,
20th and Northampton Streets,
Easton, Pa.

Editor.....C. C. DAVIS
Advertising Manager.....E. R. BRIDGWATER
Associate Advertising Manager.....S. E. BYAM
Secretary-Treasurer.....H. E. SIMMONS

Vol. VII April, 1934 No. 2

CONTENTS

General Subjects

PAGE
Rubber Division Activities..... xiii
New Books and Other Publications..... xv

Reprinted Papers

The Proöxygenic Role of Iron in the Oxidizability of Rubber. By CHARLES DUFRAISSE and ROGER VIEILLEFOSSE..... 213

Oil-Resisting Rubber. By W. J. S. NAUNTON, MALDWYN JONES, and W. F. SMITH..... 234

The Plastic Properties of Several Types of Unvulcanized Rubber Stocks at High Rates of Shear. By J. H. DILLON and N. JOHNSTON..... 248

The Effect of Temperature on the Plasticity of Rubber. By R. D. PRESTWICH..... 265

The Physical Structure of Elastic Colloids. By W. F. BUSSE..... 273

The Resistance of Anisotropic Rubber Sheets to Cutting and to Tearing. By F. KIRCHHOF..... 289

Solution Properties of Dried Rubber. By T. H. MESSENGER..... 297

Investigation of the Aging Processes in Rubber. By B. DOGADKIN and G. PANTSCHENKOW..... 302

The Russell Effect with Rubber. By A. VAN ROSSEM and J. H. E. HESSELS..... 309

The Electro-deposition of Rubber on a Zinc Anode. By B. DOGADKIN and D. SANDOMIRSKY..... 314

Entered as second-class matter May 12, 1928, at the Post-Office at Easton, Pennsylvania, under the Act of August 24, 1912.

The Preparation of Chlorinated Rubbers from Latex. Hypochlorination and Chlorination Processes. By G. F. Bloomfield and E. H. Farmer..... 320

The Action of Hypochlorous Acid on Rubber. By G. F. Bloomfield and E. H. Farmer..... 327

Textile Finishes Research. By H. P. Stevens..... 330

Effect of Temperature and Frequency on the Dielectric Constant, Power Factor, and Conductivity of Compounds of Purified Rubber and Sulfur. By A. H. Scott, A. T. McPherson, and Harvey L. Curtis..... 342

Effect of Temperature on Tensile Properties of Vulcanized Rubber. By A. A. Somerville and W. F. Russell..... 371

Mechanism of Rubber Aging. By Bernard L. Johnson and Frank K. Cameron..... 387

Effect of Oils and Chemicals on DuPrene Compounds. By O. M. Hayden and E. H. Krismann..... 393

Physical Properties of DuPrene Compounds. By E. R. Bridgwater..... 406

RUBBER CHEMISTRY AND TECHNOLOGY

Rubber Chemistry and Technology is published quarterly under the supervision of the editor representing the Rubber Division of the American Chemical Society. The object of the publication is to render available in convenient form under one cover all important and permanently valuable papers on fundamental research, technical developments, and chemical engineering problems relating to rubber or its allied substances.

Rubber Chemistry and Technology may be obtained in one of three ways:

(1) Any member of the American Chemical Society may become a member of the Rubber Division upon payment of the dues ($2.00) to the Division and thus receive Rubber Chemistry and Technology.

(2) Any one who is not a member of the American Chemical Society may become an Associate Member of the Rubber Division (and also a member of his local group if desired) upon payment of $4.00 per year to the Treasurer of the Rubber Division, and thus receive Rubber Chemistry and Technology.

(3) Companies and Libraries may subscribe to Rubber Chemistry and Technology at a subscription price of $6.00 per year.

All applications for regular or for associate membership in the Rubber Division with its privilege of receiving this publication, all correspondence about subscriptions, back numbers, changes of address, and missing numbers, and all other information or questions should be directed to the Secretary-Treasurer of the Rubber Division, Professor H. E. Simmons, Easton, Pennsylvania, or University of Akron, Akron, Ohio.

Articles, including translations and their illustrations, may be reprinted if due credit is given Rubber Chemistry and Technology.

Rubber Division Activities

The Rubber Division of the American Chemical Society

Officers

Chairman.....IRA WILLIAMS, E. I. du Pont de Nemours and Co.
Vice-Chairman.....S. M. CADWELL, United States Rubber Co.
Secretary-Treasurer.....H. E. SIMMONS, University of Akron, Akron, Ohio
Executive Committee L. B. SEBRELL, F. W. STAVELEY, J. T. BLAKE, H. J. CONROY, CARL FRICK
Sergeant-at-Arms.....C. W. CHRISTENSEN

Meeting of the Rubber Division of the American Chemical Society at St. Petersburg, Florida, March 28–29, 1934

The meeting was held in the ballroom of the Soreno Hotel, with sixty-two in attendance at the first session.

The program was as follows:

Morning Session of March 28

1. L. B. Sebrell and Winfield Scott. The Mechanism of the Action of Organic Accelerators in the Vulcanization of Rubber.
2. Waldo L. Semon. The Use of Age-Resistors for Retarding the Deterioration of Rubber.
3. A. R. Kemp and F. S. Malm. The Chemistry of Hard Rubber (Ebonite).

Morning Session of March 29

4. J. McGavack and J. S. Rumbold. The Presence of Alanine in Rubber Latex.
5. Harold Gray, H. S. Karch, and R. J. Hull. A Method for Determining Flex-Cracking in Treads.
6. Ira Williams. The Relation of Volume Change to the Mechanism of Vulcanization of Rubber.

Business Meeting.

The dinner was held on the evening of March 28 in the ballroom of the Soreno Hotel as a joint dinner with the Paint and Varnish Division. Eighty-five were in attendance at the dinner, which was arranged by a Committee composed of H. G. Bimmerman and C. A. Bartel.

The beautiful prizes, which were awarded by drawing, were made possible by gifts of money from Binney & Smith, American Cyanamid and Chemical Co., General Atlas Co., United Carbon Co., Krebs Pigment and Chemical Co., E. I. du Pont Co., R. T. Vanderbilt Co., Rubber Service Laboratories, and the New Jersey Zinc Company.

The Secretary made the following report which, upon motion, duly made and carried, was ordered a part of the minutes.

Secretary's Report

Total membership to date (March 24, 1934)...		359
Members paid for 1934.....	250	
Associate members paid for 1934.....	72	
New members for 1934.....	37	
Total membership not paid.....		100
Members not paid for 1934.....	70	
Associate members not paid for 1934.....	23	
New members in 1933 not renewed for 1934..	7	
Subscriptions paid for 1934.....		87
Old subscriptions renewed.....	75	
New subscriptions for 1934.....	12	
Subscriptions not renewed for 1934.....		20
New subscribers in 1933, not renewed for 1934..		1
Honorary members and exchanges.....		32

The Treasurer's report was read and approved, and is hereby made a part of the minutes:

Treasurer's Report

Balance in bank at the Chicago meeting, Sept., 1933.....		$ 735.72
Received from dues and subscriptions.....		1294.95
Received from advertising.....		1614.09
Received from surplus at the Chicago banquet (Frick)...		70.40
Received from Rubber Manufacturers' Association.....		1500.00
		$5215.16
Expenditures		
Mack Printing Co. (July and October issues).....	$1773.81	
Translations and index.....	139.45	
Typewriter, postage, etc., for C. C. Davis' office.....	83.40	
Printing and envelopes for circular letter.....	55.50	
Expenses of Secretary-Treasurer to Chicago meeting.....	68.48	
Secretarial Services (6 months).....	60.00	
Postage (Journals to foreign countries) office supplies, telephone and telegrams.....	13.38	
Debit of English check.....	0.20	
Tax on checks written.....	0.30	
	$2194.52	
Balance in bank at St. Petersburg meeting.....		$3020.64
Money in liquidation bank.....	$2436.05	
Money for advertising in Jan. issue of RUBBER CHEMISTRY & TECHNOLOGY.....	266.05	2702.10
Total.....		$5722.74

Upon motion meeting adjourned.

H. E. SIMMONS, *Secretary-Treasurer*

New Books and Other Publications

Fifteenth Report on Native Rubber Cultivation. By A. Luytjes and C. J. van Bijlert. Published by the Bureau of Agricultural Economics, Buitenzorg, Java. 16 pp. 1933.

Detailed figures of production in the Netherlands East Indies are carried through the second quarter of 1933 in this report. A chart is included to show the trend of production or export from leading sources from 1931 to 1933. [From *The Rubber Age* of New York.]

Sixteenth Report on Native Rubber Cultivation. By A. Luytjes and C. J. van Bijlert. Published by the Bureau of Agricultural Economics, Buitenzorg, Java. 8 pp. 1933.

Results of the increased price for crude rubber on native output are shown in this report. Its figures and tables for production in the Netherlands East Indies are carried through the third quarter of 1933. [From *The Rubber Age* of New York.]

"Taschenbuch 1934 für Gummitechniker." ("Pocket Handbook for Rubber Technologists, 1934.") In this book Werner Esch presents useful technical data in a number of articles as "The Effect of Varying Carbon Black Doses and Varying Heating Periods;" "Effect of Latex Preparations on Rubber Vulcanizates;" "Sprayable Rubber Solutions;" "Cementing Rubber Vulcanizates on to Iron;" "Rubber Types as Adhesives." The data in "Production of Varnishes for Galoshes Using Linseed Oil" are rather antiquated. A descriptive list of compounding ingredients and various tables complete this handy little book. [From the *India Rubber World.*]

Book of A. S. T. M. Standards. Part I, Metals, 1000 pp. Part II, Non-Metallic Materials, 1300 pp. 1933. Either part, $7.50; both parts, $14.

Book of A. S. T. M. Tentative Standards. 1140 pp. 1933. $7.

Index to A. S. T. M. Standards and Tentative Standards. 124 pp. 1933. For free distribution.

These volumes, issued by the American Society for Testing Materials, Philadelphia, Pa., are, of course, essential to manufacturers, designers, and engineers who must have access to the standard specifications, methods of testing, definitions of terms and recommended practices contained in their pages. Of the adopted standards, those contained in Part II on Non-Metallic Materials are of greatest interest to rubber technologists inasmuch as this volume includes those relating to rubber products, textiles, and electrical insulating materials. The 1933 Book of Tentative Standards has 40 items in these three groups. The Index covers these volumes as well as the *Proceedings* of the Society and is valuable for ready reference. [From *The Rubber Age* of New York.]

Rubber Flooring and Furnishings. Published by the Rubber Growers' Association, Inc., London. 26 pp. 1933. For free distribution.

Until a few years ago, rubber was not considered seriously for interior furnishing. Today, however, improvements have made rubber flooring popular and are beginning to establish a place for rubber panelling, rubber-backed carpeting and even upholstery of latex sponge or latex-treated hair. Such uses are even more general in England than in this country, and typical examples are illustrated in the pages of this reprint. [From *The Rubber Age* of New York.]

Trends of Manufacturing Costs in the Automobile Tire and Inner Tube Industry, 1914 to 1931. Published by the Rubber Division, U. S. Department of Commerce, Washington, D. C. 20 pp. 1933.

While costs of materials and labor show declines for the tire industry from 1923 to 1929, other costs, which include fixed charges, overhead, salaries, and profits, record a sharp advance. This "other costs" element of expense is, therefore, the only one which has been steadily rising, and in the tire industry it ranked in importance equal almost to materials in 1931. [From *The Rubber Age* of New York.]

"The Protection by Patents of Scientific Discoveries." Report of the Committee on Patents, Copyrights, and Trade Marks. By Joseph Rossman, chairman, F. G. Cottrell, A. W. Hull, and A. F. Woods. Supplement to *Science*, No. 1, January, 1934, Volume 79. The Science Press, New York, N. Y. Price 50 cents. This report consists of 2 parts: Part I. Should Scientific Investigators Obtain Patents? Part II. The Protection of Scientific Property. This very thorough study is interspersed with summaries and conclusions on the topics treated. [From the *India Rubber World.*]

Safeguarding Industry Against the Pilfering of Ideas. By Henry Creange. Published by George Grady Press, 445 West 41st Street, New York City. 76 pp. 1934. $1.50.

To some extent design piracy has been felt by the rubber manufacturing industry, and legislation such as the author advocates to declare this an unfair form of competition would probably be welcomed by many manufacturers. Mr. Creange, known as technical adviser to industries here and abroad, explains how one may know the "parentage" of a design and discusses the steps taken in France and other countries to protect the originators of ideas. [From *The Rubber Age* of New York.]

Annuario delle Materie Plastiche. Published by P. A. Pollini, Via Torino, 47, Milan, Italy. 432 pp. 1934. 20 lire.

Formerly issued as a part of a combined Rubber and Plastics Year Book, this volume is now published separately for the plastics industries. It contains a wealth of material on the manufacture of plastic products and is copiously illustrated. A 1934 Italian Rubber Year Book will be issued by the same publisher later this year. [From *The Rubber Age* of New York.]

Silicosis. Published by the Industrial Health Section, Metropolitan Life Insurance Company, 1 Madison Avenue, New York City. 32 pp. 1933. For free distribution.

Finely ground silica of all types is employed as a filler in rubber, hard rubber, pressed and molded goods. Recognition of the harmfulness of silica dust to the lungs of workers and the taking of steps toward dust prevention should, therefore, be important to rubber company plant superintendents and safety directors. Suggestions in this booklet should be of distinct aid in controlling dusty processes arising in the course of manufacture. [From *The Rubber Age* of New York.]

"The Story of the Tire." The Goodyear Tire & Rubber Co., Inc., Akron, O. This book of 48 pages is the fifth edition of "The Story of Goodyear." The fascinating account of rubber, cotton, and their processing into modern pneumatic tires is one of absorbing interest not only for the technical information conveyed to the reader, but for the insight afforded of the foresight and success with which Goodyear has developed and coördinated its world-wide facilities for manufacturing and merchandising its enormous output of tires and tubes, mechanical rubber goods, and aircraft. [From the *India Rubber World.*]

Rubber and Automobiles. By Colin Macbeth, with foreword by F. W. Lanchester. Published by the Rubber Growers' Association, Inc., 2 Idol Lane, Eastcheap, London, E. C. 4, England. 132 pp. February, 1934. Free on application (postage 4½ d.).

This is the second edition of a volume which first appeared in May, 1933. Additional information is now provided on rubber suspension systems, sliding spring shackles, rubber bumpers which act as stabilizers, engine and radiator mountings, crank-shaft bushings, steering wheel horn rings, door hinges, rubber seatings and latest types of leak-proof moldings for coach bodies. A more comprehensive index is included, and illustrations of the new items mentioned are presented, together with a frontispiece depicting rubber usage on the modern car. The book is bound in a loose-leaf cover to permit the inclusion of additional material. [From *The Rubber Age* of New York.]

Rubber: Report A-9. Published by the National Association of Purchasing Agents, 11 Park Place, New York City. 28 pp. March, 1934.

The intent of this report is to present a fairly complete survey of conditions existing in the rubber industry for the benefit of the purchasing agent who is assigned the duty of buying this commodity. After a general discussion of the growing and manufacture of rubber, details of packing, prices, specifications, statistics and sources of information are provided. Particularly helpful are personal purchase practice opinions and suggestions by ten representative buyers of crude rubber. [From *The Rubber Age* of New York.]

[A translation for Rubber Chemistry and Technology of a hitherto unpublished paper.]

The Proöxygenic Role of Iron in the Oxidizability of Rubber

Charles Dufraisse and Roger Vieillefosse

LABORATORY OF ORGANIC CHEMISTRY, COLLÈGE DE FRANCE, PARIS

I. THEORETICAL PART

The influence of iron on the oxidizability of rubber, though not as a matter of fact neglected in the past, has perhaps not received sufficient attention.

However, the various ways in which this metal and its derivatives have caused contamination are certainly too obvious to imagine that they have passed unobserved.

As is known,[8,14] traces of iron can be detected in latex at the time it is tapped, and regardless of the method of treatment which it undergoes later, the rubber has an opportunity at every step in its preparation to become further contaminated with iron. Milling, calendering, and molding are carried out with iron equipment, and the ingredients used in rubber compounding may contain more or less iron, at least as impurities, even when they are not primarily iron compounds, as is the case of certain pigments. In short, manufacturing processes, contamination by iron from ingredients, adventious causes such as iron containers for latex,[8] dust and various other causes which need not be enumerated, all contribute to the presence of iron in rubber.

Certainly then iron cannot be a very dangerous element under ordinary conditions, for otherwise its harmful effects would have been recognized long ago, and would have led to the avoidance of iron in practice, as has happened in the case of copper.

Nevertheless experiments of the authors to determine why vulcanization increases the oxidizability of rubber have led to the suspicion that iron may be harmful, and a desire to ascertain the role it plays in deterioration prompted the authors to carry out the experiments which are described in the present paper.

The object of the work was thus limited, and it aimed not to settle the problem of the influence of iron on rubber, but rather to investigate in a simple manner in what way iron gets into a rubber mixture, in what form it exists, and what are its harmful effects. Incidental to this, some of the observations may perhaps be of some value in current practice.

A. Historical

It appears that Thomson and Lewis[1] in 1891 were the first to call attention to the influence of iron as well as that of copper and manganese on the oxidizability of rubber. Weber[2] in 1898 mentioned the harmful action of the chloride, Fickendey[3] and Eaton[4] that of iron salts, and Frank[5] that of the free element.

Subsequent to various tests of Marx and Zimmerman[6] on the effect of the chloride on manihot, and of Morron and Webster[7] with Prussian blue, van Rossem and Dekker[8] in 1926 showed the presence of 0.006 per cent of natural iron in rubber, and also called attention to the high content in latex shipped to Europe in tinned iron containers.

Kirchhof[9] described the tackiness and hardening brought about by several salts of iron, while Taylor and Jones,[10] as a result of tests on the effect of different metals in the form of stearates, classified in their order of diminishing activity:

copper, manganese, and iron, with a threshold of activity of 0.5 per cent for iron. This investigation was extended to include jelutong by Georgi.[11]

Scott[12] studied the effects of Prussian blue and of ferrocyanides, and in 1931 in a detailed study of the effect of manganese Kirchhof[14] mentioned the presence of iron in rubber in quantities which varied greatly with the origin of the rubber, *viz.*, from 0.01 to 0.6 per cent in certain brown Congo rubbers. According to Kirchhof, iron and manganese have a mutual activating effect in supplying oxygen.

In 1932 Ayers[15] described a proöxygenic action of ferric sulfate present in iron oxide as a result of incomplete washing, and in 1933 Freundlich and Talalay[17] mentioned the deteriorating effect of ferric chloride. In connection with a general investigation of the autoöxidation of rubber in latex, Stevens[18] observed the decomposition of latex kept in iron containers for long periods of time. On the contrary, ferric oxides used as pigments brought about deterioration only under hot conditions and after long storage.

It is well to call attention to the fact that numerous other substances are sensitive to the proöxygenic action of iron or its compounds (see among other authors: Dufraisse and Horclois[13] for various substances, Franke[16] for unsaturated fatty acids, etc.).

Finally attention should be called to the fact that, under some conditions, certain derivatives of iron have shown antioxygenic properties rather than a tendency to accelerate oxidation (cf. Dufraisse and Horclois[13]).

B. Iron Naturally Present in Rubber

The proportion of iron naturally present in rubber is always very low, and a relatively sensitive method must be used to determine it. In the present work a colorimetric method with ferric thiocyanate was used.

The determination as such involves no difficulties. Nevertheless the preliminary incineration, which is a necessary step, is both a long and tedious operation, for relatively large masses of rubber must be destroyed in order to obtain enough ash to determine the iron. Moreover unremitting care is necessary to avoid loss by entrainment of particles.

Because of having to carry out a large number of these determinations, a very simple method was developed for destroying the organic matter by combustion in oxygen. Since this technic gave good results in service, it was believed that it might be helpful to describe it in the Experimental Section, particularly since it is suitable for the determination of any fixed matter in general.

Various types of crude rubber were examined by this method, including first latex crepe, smoked sheet, coagulated "Jatex", and latex evaporated to dryness. The sample of latex was obtained from the plantation and was shipped in a glass container and out of contact with any metal.[24]

Table I shows the iron determinations, which vary from 0.002 to 0.006 per cent. These values are in good agreement with those of van Rossem and Dekker[8] and of Kirchhof.[14]

C. Iron Taken from the Mill during Mixing

Contrary to what might be supposed of a material so lacking in hardness as rubber, notable quantities of iron are removed from the rolls during the mixing operation.

(*a*) *Conditions under Which Iron Is Removed.*—Pale crepe and coagulated Jatex were masticated for a long time on a laboratory mixing mill, and samples were removed at regular intervals for testing. In each case, the iron was determined, as

well as the viscosity in benzene solution, in order to follow the changes with the mechanical treatment.

From Fig. 1, which summarizes the results of the measurements, and from Tables II and III, it is seen that the iron content increases in a regular manner with the progress of mastication,[25] with no evidence of any tendency to approach limiting values.

Furthermore after a given mechanical treatment, the abrasive action of crepe was less than that of Jatex, which is far more firm, doubtless because of the process for coagulating it which was used in the present work.

By repeating these tests numerous times, it was proved that there were in the individual experiments large variations in the quantities of iron removed from the mixing rolls by the same rubber subjected to the same mechanical treatment. With crepe masticated in the normal way, the proportions of iron varied from 0.02 to 0.10 per cent, representing products varying in color from pale to an approach to black.

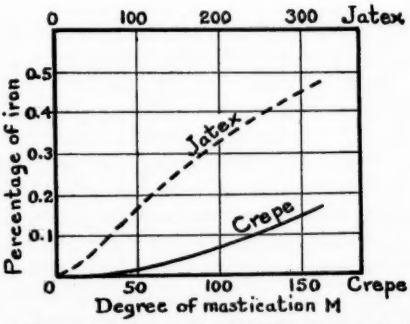

Figure 1—Increase in the Iron Content of Rubber with the Degree of Mastication on a Laboratory Mill

The curves represent data in Tables II and III.

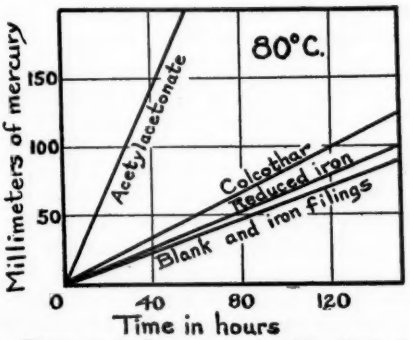

Figure 2—Influence of 0.1 Per Cent of Iron, in Different Forms, on the Oxidizability of an Unvulcanized Mixture of Crepe with 6 Per Cent of Sulfur. The Viscosities Were from 9.8 to 11.8 Seconds, Expressed as Times of Flow in a Pipette

These differences, the exact cause of which is difficult to establish, must be attributed to variations in temperature, tightness of the mixing rolls, atmospheric humidity and electrical phenomena, and doubtless also to the manner in which the rubber was worked on the mill.

Whatever may be the explanation, the milling operation introduces into the rubber quantities of iron which are anything but negligible, since they may reach fifty times the quantity originally present. Moreover the attack upon the rolls is continuous, and does not diminish as the operation continues, even though the rubber becomes progressively softer. "Dead-milled" rubber reaches an iron content of more than 0.1 per cent.

With large factory machines, the same phenomenon is encountered, though to a somewhat less degree (see Table IV), without doubt because the mutual friction of the rolls is less pronounced.

(*b*) *State of the Iron in the Masticated Rubber.*—An investigation was carried out to ascertain whether the iron thus introduced by milling remained as the free element or whether it existed in the combined state.

The first experiments were concerned with the question whether the iron was dissolved. To this end, a large sample of masticated crepe, containing an appreci-

able quantity of iron, was dissolved in benzene, and then let stand in darkness for two months. The liquid became progressively clearer as a result of the deposition of a black powder. The liquid was then decanted and centrifuged energetically in order to collect as much as possible of the precipitate.

The iron which was thus separated in an insoluble form represented approximately four-fifths of the total iron. However, the remaining one-fifth was not necessarily in the dissolved state, because the viscosity of the liquid offered resistance to the complete precipitation of all the particles in suspension. This was evident by microscopic examination of a thin film obtained by evaporation of a fraction of the solution centrifuged for a long time. Fine solid particles were still visible, though not in sufficient quantity to account for the remaining one-fifth mentioned above. It was therefore justifiable to assume that a small quantity of metal, twenty per cent at the maximum, was in the dissolved state, *i. e.*, in the combined state.

As for the insoluble iron in the precipitate, it was no longer in the free state, in fact the deposit obtained by decantation and centrifuging dissolved in hot hydrochloric acid, without liberation of hydrogen, and moreover it contained only 40 per cent of the metal.

Two-thirds of the residue, or 40 per cent of the total, was composed of combustible organic material, while the final one-third, or 20 per cent of the total, was by difference doubtless inorganic matter and oxygen combined with the metal.

In brief, in the experiment described, all of the iron introduced into the rubber by milling becomes combined, the major part, *i. e.*, at least 80 per cent, is in the dispersed state, while 20 per cent more may be found in solution in an organic form.

Just as great differences were found among the individual values for the total iron, there should in all probability be similar large variations in the proportions of the iron dissolved in the rubber. Thus some other samples which contained less iron than the preceding one, *i. e.*, about five times the original proportion, were of relatively much lighter color, which would indicate that in these samples the metal was to a large extent in solution, for it is in the state of pigment in the undissolved or microscopically visible ("figuré") state that iron gives a black coloration, not in the dissolved state, where at low concentrations its color is insignificant.

The series of centrifugings, which was very long, was not repeated, because the form in which the metal is introduced into the rubber before vulcanization is of only secondary importance from a practical point of view, as will be seen from what follows.

D. The Effect of Iron on the Oxidizability of Rubber

The first tests were made with latex, *i. e.*, Jatex, but this was abandoned because it was found impracticable to develop a technic which would consistently give coagulated samples of the same oxidizability. Plantation pale crepe was accordingly used.

Whereas with latex the iron or iron salts could be incorporated directly into the mass without any additional operations, crepe required either mechanical treatment (mastication) or swelling in solvents. These operations might be thought to have an effect on its affinity for oxygen, but this was found not to be the case by experiments with control samples which had undergone the same physical treatment as the samples to which iron had been added. In so far as the mastication was concerned, identical conditions were maintained by carrying out the operations consecutively for the same time on the same mill rolls, spaced in the same way, with the same quantity of rubber. As a control test, the viscosities

of benzene solutions of the samples were compared, a test which is very sensitive to the degree of mastication.

This study was carried out with reduced iron, iron filings, colcothar, Venetian red, Prussian blue, potassium ferrocyanide, iron acetylacetonate, ferric chloride, and ferric sulfate. The influence of these reagents was studied, both on raw rubber and on vulcanized rubber, in the latter case almost always without an accelerator, *viz.*, in a mixture of rubber 100 parts, sulfur 6 parts.

Figs. 2 to 20 give the results of these tests and show the consistent proöxygenic character of iron, as well as the extreme variability in its activity according to the state in which it exists.

Reduced iron and iron filings were almost inert (see Figs. 2, 4, and 7). Certain inorganic compounds, such as Prussian blue (see Figs. 3, 4, and 6), colcothar, and Venetian red (see Figs. 2, 3, 4, 5, and 7) were a little more active. Venetian red, which is sometimes employed as a pigment, doubled the oxidizability of vulcanized rubber, even when only one per cent (calculated as iron) was present.

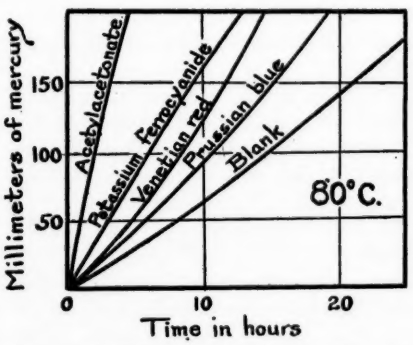

Figure 3—Influence of 0.1 Per Cent of Iron, in Different Forms, on the Oxidizability of a Mixture of Crepe with 6 Per Cent Sulfur, Vulcanized for 3.5 Hours at 3.5 Kilograms' Pressure. At the End of the Mixing, the Viscosities Were from 6 to 6.6 Seconds, Expressed as Times of Flow in a Pipette

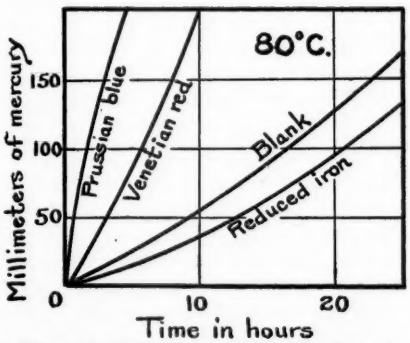

Figure 4— Influence of 1 Per Cent Iron, in Different Forms, on the Oxidizability of a Mixture of Crepe with 6 Per Cent Sulfur, Vulcanized 3.5 Hours at 3.5 Kilograms' Pressure. At the End of the Mixing the Viscosities Were from 6.2 to 7.2 Seconds, Expressed as Times of Flow in a Pipette, Except for the Mixture Containing Venetian Red, in Which Case the Viscosity Was Not Measured

The activity of Prussian blue, which has already been reported by Scott,[12] was almost the same as that of Venetian red, *i. e.*, with one per cent (calculated as iron) the acceleration of oxidation may become as high as five-fold (see Fig. 4). Potassium ferrocyanide had much the same activity as the preceding substances (see Figs. 3 and 5). Finally ferric chloride (see Fig. 15) and particularly the acetylacetonate (see Figs. 2, 3, and 8 to 19) are to be considered in a wholly separate category, *i. e.*, as energetic proöxygens.

E. Special Study of the Effect of Iron Acetylacetonate

Because of the disturbing activity of the acetylacetonate, a more thorough study was considered necessary to ascertain under what conditions iron may be found in its harmful forms, and at the same time to determine the extent of this danger.

(*a*) *Threshold of Its Activity.*—When introduced, by diffusion, in increasing proportions into raw crepe (see Fig. 8), the acetylacetonate increases the oxidizability of the crepe at first slowly, then much more rapidly, up to a content corresponding

to about 0.15 per cent of iron, above which the activity appears to diminish. In this last range, it is probable that the slowness of diffusion of the oxygen through the mass plays a part in the process.

The curves on a much larger scale in Fig. 9, which correspond to the lower proportions of acetylacetonate, show that its *threshold of activity lies at approximately 0.01 per cent* (calculated as iron), *i. e., one ten-thousandth part of iron.* It was proved that the "carrier" of the iron, *viz.*, acetylacetone, has no proöxygenic effect (see Fig. 18), and the effect is therefore to be ascribed to the iron itself, the role of the "carrier" being only to confer upon the iron an active form.

(*b*) *Influence of the Method of Incorporation.*—All the forms of iron studied up to this point were introduced into the rubber by milling, whereas the acetylacetonate in this last experiment was incorporated by diffusion. The question thus arose whether this was the cause of its exceptional activity.

To settle this question, comparative tests by milling and by diffusion were carried out. Two mixtures of the same composition, which had undergone the same treatment, differed only in the manner in which the reagent was introduced, *i. e.*, in one case by impregnation before mastication, and in the other case by ordinary incorporation directly during mastication. Fig. 17, which represents mixtures containing 6 per cent of sulfur, both before and after vulcanization, shows no notable differences in the results by the two processes.

Judged by their simple form, the curves in Fig. 10, which represent experiments with increasing times of mastication, seem to indicate that as the incorporation of the acetylacetonate progresses, there is a corresponding increase in the activity, an activity which is ultimately limited by the destruction of the product (see curves corresponding to 40 minutes). Nevertheless this is a difficult question to settle because high rates of oxidation are involved, with a resulting uncertainty about the rate of diffusion of oxygen through the mass.

(*c*) *Influence of Sulfur and of Vulcanization.*—The presence of sulfur in a mixture reduces notably the effectiveness of the acetylacetonate, which may be ascribed to the conversion of the catalyst to a less active sulfurated form. Thus merely by milling rubber in the cold with 6 per cent of sulfur (see Fig. 17, curves 3 and 4), the oxidizability in the presence of 0.1 per cent of iron is reduced to one-half of its value compared to the oxidizability without sulfur (see Fig. 8, middle curve).

An elevation of the temperature accentuates the phenomenon, as is evident from the curves of oxidation at 80° C. of raw mixtures containing sulfur. The angular coefficients, representing rates of oxidation, diminish progressively with increase in the time of oxidation (see Fig. 11, curves with broken lines; Fig. 17, curves 3 and 4; Fig. 12). This change is not to be attributed to a secondary effect of the oxidation, for it does not take place in the absence of sulfur (see Fig. 11, solid curves).

Moreover simply by storage at room temperature, rubber-sulfur mixtures which were at first rose-colored because of the iron reagent lost this color after several days showing that some internal reaction takes place.

According to all this, one would expect that vulcanization without an accelerator would bring about a more pronounced modification in the effectiveness, because of the prolonged heating (3.5 hours) and the high temperature (143° C.) required. As a matter of fact heating in the presence of sulfur greatly reduces the activity of the acetylacetonate. This is already evident (see Fig. 3) where the addition of 0.1 per cent (calculated as iron), before vulcanization, increases the oxidizability only six-fold compared to the control sample. On the other hand, in the absence of

sulfur, the same addition increases the rate of oxidation of raw crepe one hundred-fold (see Figs. 8 and 9).

In order to verify whether the phenomenon is a chemical reaction between the two reagents during the heating and is not a true insensitivity in the vulcanized state, the catalyst was introduced by diffusion after vulcanization. Its activity was thus reëstablished, as is evident from a comparison of Figs. 13 and 14.[26]

In these experiments, the increase in activity is in part masked, because the rate of oxidation is great enough to be noticeably retarded by the slowness of penetration of oxygen into the interior of the rubber.

This retardation of the rate of oxidation as the proportion of catalyst increases is evident in Fig. 12. The oxidizability does not increase in proportion to the percentage of catalyst. It is therefore preferable to work with smaller proportions.

With 0.025 per cent (as metal) there was an increase in the rate of oxidation of about six times, compared with the control sample (see Fig. 12), that is to say, comparable to the increase found for raw crepe in the absence of sulfur. There is an even more pronounced effect relatively, namely, a coefficient of acceleration of

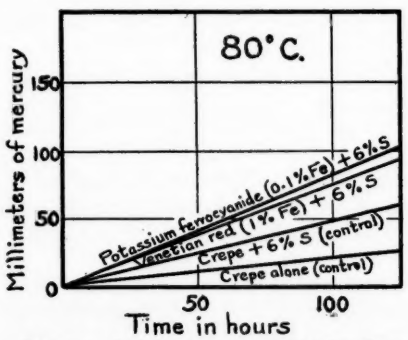

Figure 5—Influence of 0.1 and 1.0 Per Cent of Iron in Different Forms on the Oxidizability of an Unvulcanized Mixture of Crepe with 6 Per Cent Sulfur. The Viscosities Were from 6.2 to 6.9 Seconds Expressed as Times of Flow in a Pipette

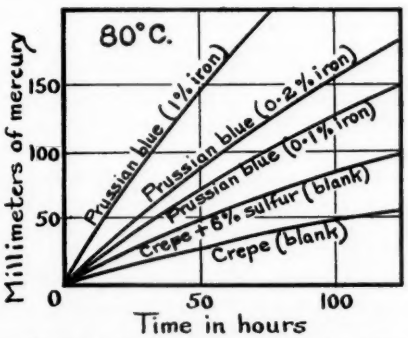

Figure 6—Influence of 0.1, 0.2 and 1.0 Per Cent of Iron, in the Form of Prussian Blue, on the Oxidizability of an Unvulcanized Mixture of Crepe with 6 Per Cent Sulfur. The Viscosities Were from 6.2 to 7.2 Seconds, Expressed as Times of Flow in a Pipette

6, with an addition of 0.016 per cent (calculated as iron) to a mixture accelerated with diphenylguanidine (see Fig. 15). It is seen on the same diagram that iron is less active in the form of ferric chloride.

Finally the existence of a reaction between uncombined sulfur and the catalyst is manifest by a concavity in the graphs, which represents a progressive diminution of the rate of oxidation (see Fig. 12), as in the case of unvulcanized mixtures.

In summary, two facts stand forth clearly as a result of this investigation:

(1) Certain forms of iron are particularly deleterious to rubber, *e. g.*, in relatively low concentrations (0.001 of metal) the acetylacetonate of iron increases by one hundred-fold the rate of oxidation of crepe. With a substance which is itself very readily oxidized, *viz.*, simple vulcanized rubber, the rate of oxidation increases to such an extent that it exceeds the rate of penetration of oxygen into the mass. The absorption of gas becomes so rapid at 80° C. that the ascent of the mercury in the manometer tube becomes visible.[27]

(2) Sulfur has a strong protective action against the active acetylacetonate form of iron, probably because it transforms it into the sulfide, which is a catalyst

with only one-tenth of the activity at the most. This effect is particularly evident after heating.

In this way vulcanization has a beneficial or purifying effect of some kind on rubber, doubtless because it transforms to the state of the less active sulfide harmful compounds of iron which the rubber may contain.

This conversion of various iron compounds to a homogeneous state makes one lose his chief interest in knowing under what forms the metal is originally present in rubber mixtures. All indications lead to the belief that after vulcanization the various forms originally present tend to give a single catalyst, *viz.*, the sulfide, the activity of which depends upon its state of subdivision within the mass.

This condition is no longer true if the rubber becomes contaminated *after it has been vulcanized*, and in this case an intensely active oxidative catalysis may again be observed.

F. Comparison of the Proöxygenic Activity of Iron and That of Copper and of Manganese

From a theoretical point of view alone, it would have been of interest to continue the work with a study of the greatest variety of iron compounds. However, this was not included in the present work.

The results above appeared to be sufficient for the immediate objective of this investigation. This objective was attained on the one hand by discovering the existence of highly deleterious derivatives of iron and on the other hand by establishing the exact conditions under which they are or are not dangerous.

For this reason further work was unnecessary. Nevertheless it was decided to make some comparative experiments with manganese and copper, which are known to have a very harmful effect, in order to determine how to classify iron in relation to them.

The acetylacetonates of the three metals were added in increasing amounts to raw crepe by diffusion by means of ether in the case of iron and manganese, and chloroform in the case of copper. Under these conditions (see Fig. 18) the proöxygenic action of iron was only one-half that of copper and only one twenty-fifth that of manganese at the most.

Another series of experiments was carried out with the same salts, but this time they were added by milling and in the presence of 6 per cent of sulfur. Here too sulfur was found to have a protective effect, as was described earlier in the case of iron. Manganese and copper are even more sensitive to the effect than is iron, to the extent that their order of activity is reversed, so that iron becomes the most active (see Fig. 19) in raw mixtures as well as in vulcanized mixtures.

According to these preliminary experiments, iron, which has the reputation of being less harmful to rubber than copper and manganese, would seem on the contrary to be more harmful than they are in the presence of sulfur, that is to say, under ordinary conditions of usage. This is a phenomenon, the consequences of which should not be ignored by technologists.

In reality, when sulfur is introduced, the three metals are equally undesirable, and one can no longer be disregarded more than another. The thing to be considered is not their nature but their state of subdivision, since the latter is the chief source of the harmful effect. This is plainly evident in Fig. 20, which represents iron and copper added by milling in the form of sulfates, consequently far less finely divided than in the form of the soluble acetylacetonates, and with correspondingly weak activities. Iron should therefore be avoided to the same extent as is copper or manganese and, as seems paradoxical, traces of iron introduced as organic impuri-

ties by compounding ingredients may be more harmful than certain large quantities introduced in the form of insoluble compounds in hydrocarbons and in compact particles.

G. The Harmful Effect of Iron under Practical Conditions

It is now time to ask, on the basis of the preceding results, what part iron plays in the ordinary deterioration of rubber when there is no contamination in some abnormal way.

The iron naturally in rubber must be disregarded. In the proportion in which it is found, even if it were in a form as active as in the acetylacetonate state, it would have no appreciable effect, since it does not reach the threshold of activity. On the other hand, one can no longer consider as negligible the quantity of the metal removed from the rolls, when this reaches 0.15 per cent in one of the experiments, *i. e.*, more than is required under certain conditions to cause serious damage.

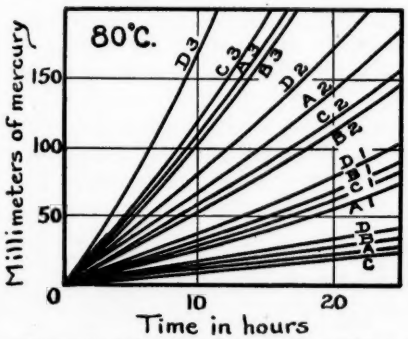

Figure 7—Influence of 0.1 Per Cent of Iron in Different Forms on the Oxidizability of a Mixture of Crepe with 6 Per Cent Sulfur, in the Raw State and Vulcanized for Increasing Times at 3.5 Kilograms' Pressure

Sample	Raw	Vulcanized at 3.5 kilograms		
		1 hr.	2 hrs.	4 hrs.
Control (blank)	A	A1	A2	A3
Reduced iron	B	B1	B2	B3
Iron filings	C	C1	C2	C3
Colcothar	D	D1	D2	D3

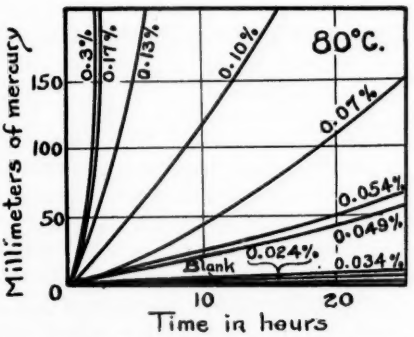

Figure 8—Influence of Iron Acetylacetonate, Introduced by Diffusion, on the Oxidizability of Raw Crepe. The Percentages Are Expressed in Terms of the Actual Metallic Iron

However, the chief cause of the deterioration of vulcanized rubber is not to be found in this way, as had been considered possible earlier. First of all, a considerable part of the iron thus introduced is combined in the undissolved ("figuré") state, in sufficiently dense particles to be precipitated from solutions even when very viscous, after standing or passing through the centrifuge. The metal, aggregated in this way, as has been seen above, has only a slight effect. Moreover, vulcanization serves to paralyze the remainder, which, because it is more finely divided or even dissolved, might be more harmful.

Iron acquired by milling does not therefore appear to be very harmful. However, it was decided to prove in a direct fashion its relative harmlessness by milling on wooden rolls, that is, with the exclusion of all metallic contact.

H. Milling on Wooden Rolls

Certain difficulties were encountered with this apparatus.

Two rolls were built of oak and mounted on a laboratory mixer. They lasted

no more than a few minutes. At the first pass the rubber penetrated deeply into the fibers. The work was continued however with the hope that the wood would smooth out by being compressed, and would finally have sufficient hardness. This did happen, but unevenly. Moreover, after several hours of milling, cracks opened up and the apparatus became useless. However, it was serviceable for a sufficiently long time to make it possible to carry out preliminary experiments.

Two new rolls were then made from guaiacum,[28] and mounted as in the preceding experiments. They gave complete satisfaction. The unusually close grain of this wood made it possible to carry out numerous millings without any appreciable change in the surface.

As might be expected in the light of recent discoveries on mixing, advantage was taken of the opportunity to study the different factors involved in this operation when wood was substituted for iron in the apparatus.

According to work by Cotton[19] and by Busse,[20] this change might affect very much the process of oxidation in air, and consequently the plasticization of rubber which is the result of this oxidation. In particular, in contact with an insulator, wood, the electric phenomena which are probably the cause of the intense reactivity of oxygen during milling are not necessarily the same as those at the surface of a metal conductor.

As a logical consequence of the present study, another possible explanation of the differences was also to be considered. Does not the actual material of which the rolls are composed, *i. e.*, iron, in virtue of its own catalytic power, take part in the plasticizing oxidation by a specific accelerating action rather than as a generator of electricity?

This is not the case. With wooden rolls mastication proceeds in the same way as with iron rolls, with this exception only, that thermal insulation prevents the mass from becoming cool, as a result of which there is considerable heating.

Other than this, there is no other phenomenon to be considered particularly. The electric phenomena are of the same intensity as usual, and the rubber becomes plasticized at a normal rate, *i. e.*, without appreciable retardation.

Accordingly, the iron in the roll does not act as an accelerator of the plasticizing oxidation. Moreover, when added intentionally, even in the most highly prooxygenic forms, it does not increase the softening of the rubber; furthermore copper and manganese have no greater effect than does iron.

This fact is of interest in connection with the chemical mechanism of the plasticizing process. It seems to suggest that the oxygen which is so energetically absorbed by rubber during milling is not ordinary molecular oxygen, otherwise the acetylacetonates of iron, copper, or manganese, which are strong catalysts of this element, would have a plasticizing effect. The oxygen which is fixed during mixing must be in a form which is altered by electric charges, and therefore it reacts either as molecules activated by displaced electrons or as separate atoms or as ozone, forms which do not react with ordinary catalysts of autoöxidation.

To return to the principal object of this investigation, it was proved that milling on wooden rolls did not modify in any accidental way the initial content of iron, since the various mixtures were tested in the usual way for their oxidizability compared with similar samples milled on iron rolls.

No differences worthy of mention were found between the two types of materials, either before or after vulcanization (see Figs. 21 and 22).

The iron removed from the rolls during milling has therefore little influence on the resistance of rubber to oxygen.

II. GENERAL RÉSUMÉ AND CONCLUSIONS

The normal presence of iron in plantation crepe which was pointed out earlier[8,14] is confirmed. The proportions are less than 0.01 per cent. The rubber from latex gathered and shipped in glass containers has virtually the same quantity of iron.

The concentration of this metal increases considerably during milling and may even reach 0.1 per cent, only a small part of which is in the dissolved state, the remainder being in particles which are precipitated from their solutions after standing or when centrifuged.

In all these forms, even the least soluble, like colcothar, iron is proöxygenic; but its activity varies considerably with its state of subdivision, and especially with the chemical nature of the compound of which it is a constituent. In quantities of 0.1 per cent in the form of acetylacetonate, it accelerates one hundred-fold

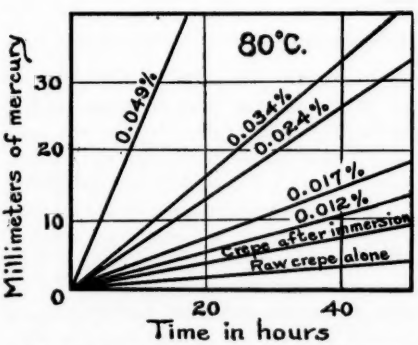

Figure 9—Influence of Iron Acetylacetonate, Introduced by Diffusion, on the Oxidizability of Raw Crepe. The Percentages Are Expressed in Terms of the Actual Metallic Iron

The first curves of Fig. 8 are reproduced on a larger scale to show the threshold of activity, which is at approximately 0.01 per cent, *i. e.*, one ten-thousandths part of iron.

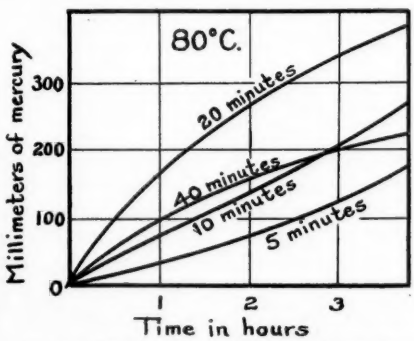

Figure 10—Influence of Milling on the Oxidizability of Raw Crepe Containing 1 Per Cent of Iron in the Form of Acetylacetonate

Sample	Time of milling in minutes	Viscosities (expressed as times of flow in a pipette) in seconds
1	5	19.5
2	10	8.5
3	20	4.6
4	40	3.5

the rate of oxidation of crepe, the threshold of activity being as low as approximately 0.01 per cent.

In the case of vulcanized rubber, which is more easily oxidized than is crepe rubber, the rate of the reaction becomes so great that it very quickly becomes limited by the slowness of the passage of oxygen through the mass, particularly if the catalyst is added after vulcanization. In spite of this, in quantities of 0.1 per cent (based on the metal) and at 80° C., the absorption of gas is so rapid that the rising of the mercury in the manometer becomes perceptible to the eye.

In the state of acetylacetonate, iron is almost as active as copper, but is twenty-five times less active than manganese.

The very active forms of iron are paralyzed by sulfur, slowly when cold and quickly when hot, a fact which is also true of copper and manganese. The consequence is that vulcanization has a curative effect on the dangerous metallic impurities, but only if contamination has taken place first.

Because of this protection, the behavior of rubber toward oxygen is only slightly

affected by the iron removed from the rolls during milling. From this point of view, milling on wooden rolls shows no very marked superiority.

All of these different experiments, considered in their relation to one another, lead to the following conclusions:

(1) In the small proportions in which it is normally found where there is no unusual source of contamination, iron is not very harmful, especially when the rubber has been vulcanized.

(2) However, when good aging qualities are desired it is advisable to avoid this metal, even in the form of derivatives as little reactive as colcothar or Venetian red.

(3) In practice, it is necessary to guard against iron compounds which may be soluble in organic solvents, such as ferric chloride or organic derivatives of iron.

(4) The unfortunate tendency to oxidize which vulcanization imparts to rubber depends to only a slight extent upon its iron content when in ordinary proportions. The cause must be sought elsewhere, and this is the object of work which is now in progress.

III. EXPERIMENTAL PART

Determination of Iron in Rubber

(*a*) *Incineration of the Rubber.*—The first experiments were carried out by burning the rubber in a platinum crucible. This was placed on an asbestos disc in such a way that the gases from the combustion of the rubber could not take fire from contact with the gas flame. This would have led, as a result of combustion of the rubber, to losses by mechanical entrainment. To avoid this particular difficulty, the rubber must be heated slowly. These precautions render the method particularly tedious; nearly an hour is necessary in order to incinerate 0.5 gram of rubber, which is the quantity generally utilized for this purpose. In view of this, the following method was adopted.

The rubber (0.5 gram) was cut into thin pieces, and packed closely in the lower part of a quartz tube with an interior diameter of 8 millimeters, and 15 centimeters long (see Fig. 23). By means of a narrow quartz tube a slow current of oxygen (approximately 100 cc. per minute) from a tank was then introduced. The delivery tube was kept 20 to 30 millimeters from the surface of the rubber, and the section of the larger tube between the point of entrance of the oxygen and the rubber was heated strongly with a Bunsen burner. The flame was then slowly brought close to the rubber, under which conditions the latter takes fire after a few seconds. The burner was then withdrawn and combustion of the rubber was maintained until the end, by letting the delivery tube from time to time approach the surface of the rubber which is burning.

If carefully carried out, this operation gives practically no smoke, no odor, and lasts about a quarter of an hour.

It has been proved by the addition of known quantities of iron that there is no loss by this method; also it usually gives percentages slightly higher than those given by the first method.

(*b*) *Solution.*—When combustion is completed and the tube is again cooled, a few cubic centimeters of pure hydrochloric acid (iron-free) are added, the tube is heated on a lukewarm water bath, and the iron solution, which is more or less yellow in color, is poured into a calibrated flask of 20 or 50 cubic centimeters' capacity, according to the estimated iron content.

This treatment is repeated several times, the quantity of iron dissolved being estimated at the beginning by the color of the successive extractions.

When solution is complete, which is after about three or four treatments with hydrochloric acid at 100° C., the volume is made up with distilled water.

(*c*) *Colorimetry.*—A comparison is made, in identical volumes of ether, of the colors of ferric thiocyanate obtained from the solution to be tested, and from a ferric solution of known titre. The latter solution is prepared with ammoniacal ferric alum, which is weighed exactly, in such a way as to obtain after dilution a solution containing 1×10^{-5} grams of iron per cubic centimeter. A series of calibrated tubes is used for carrying out the measurement. In one is mixed a solution to titrate (according to the concentration judged by the coloration); 0.5, 1, or 2 cubic centimeters.

Nitric acid (1%, free of iron)	2 cc.
Distilled water	made up to 20 cc.
Potassium thiocyanate (10% soln.)	5 cc.
Ether	10 cc.

This is stoppered and shaken vigorously until the color passes entirely into the ether layer. Several similar tubes are prepared, independently by replacing the unknown solution with volumes of the standard solution, varying by 0.25 cubic centimeters,

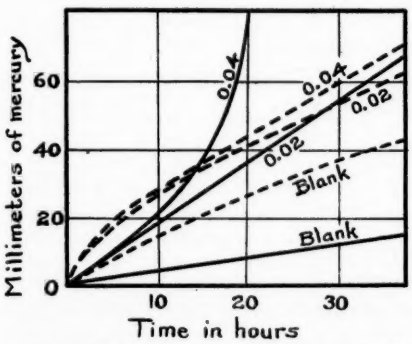

Figure 11—Influence of Different Quantities (Expressed as Percentages of Metallic Iron) of Iron Acetylacetonate, Introduced by Diffusion, on the Oxidizability of (1) Raw Crepe (Solid Lines), and (2) An Unvulcanized Mixture of Crepe with 6 Per Cent Sulfur (Broken Lines)

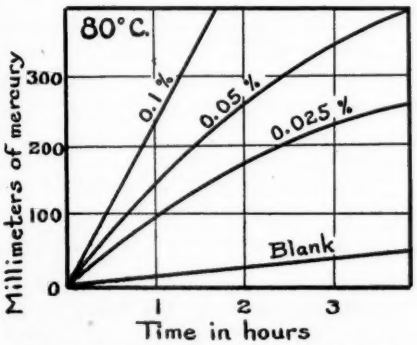

Figure 12—Influence of Different Quantities (Expressed as Percentages of Metal) of Iron Acetylacetonate, Introduced by Diffusion after Vulcanization, on the Oxidizability of a Mixture of Crepe with 6 Per Cent Sulfur, Vulcanized 3.5 Hours at 3.5 Kilograms' Pressure

i. e., 0.25×10^{-5} gram of iron from one tube to the next. The tubes are compared against a white background in bright light.

Iron Naturally Present

Table I gives the values obtained in determinations carried out on rubber in the natural state.

TABLE I

IRON IN THE NATURAL STATE IN RUBBER

Type of Rubber	Iron Content in Per Cent
First latex crepe	0.0028
First latex crepe	0.002
First latex crepe	0.006
Smoked sheet	0.0025
Jatex coagulated with acetic acid[29]	0.0022
Latex ("Third Mile") evaporated to dryness	0.002

Iron Added during Milling

Tables II and III give the values of the quantity of iron removed from the rolls during the process of milling on a laboratory mill for a sample of crepe and for a sample of coagulated Jatex.

For each of the two experiments a definite amount of rubber was used, and samples were removed at regular intervals (5 minutes in the case of the crepe and 3 minutes for Jatex).

The mechanical working increases with the time of milling, and the smaller is the mass of rubber, the more intense is this mechanical working during a given time. The time of mixing does not in itself therefore give sufficient information, and resort was had to the term *degree of mastication* M, where account was taken of both the mass of rubber and the time of milling.

Degree of Mastication

As a first approximation, all conditions being equal, it is assumed that the mechanical work which the rubber undergoes is in direct proportion to time T and is in inverse proportion to the weight P of the material treated. The degree of mastication M is accordingly defined by the equation:

$$M = \frac{T}{P} \times 1000$$

where T is expressed in seconds and P in grams.

The coefficient 1000 is introduced to avoid decimals so that the coefficient M refers to one kilogram of material.

TABLE II
(PALE CREPE)
IRON REMOVED FROM THE ROLLS BY CREPE DURING MILLING ON A LABORATORY APPARATUS

The Iron Contents Given in This Table Are the Same as Those Shown on Fig. 1

No. of Sample	Time of Milling in Minutes	Weight of Sample before Removal	Viscosities (Time of Flow in Sec.)	Degree of Mastication	Iron Content in % (Average of 2 Experiments)
C 1	3	400	3633	7	0.007
C 2	8	390	1113	20	0.012
C 3	13	380	403	33	0.009
C 4	18	370	90	47	0.016
C 5	23	360	30	61	0.017
C 6	28	350	18	75	0.027
C 7	33	340		89	0.047
C 8	38	330	9.6	104	0.050
C 9	43	320	6.8	120	0.078
C10	48	310	6	136	0.12
C11	53	300		153	0.15

When a constant mass of rubber is milled, the degree of mastication is equal to the time, except for the factor. On the contrary, if the quantity of rubber on the rolls is decreased, for example, by successive removals of samples, as in the preceding experiments, the degree of mastication at a given moment will be the sum: $M = \Sigma[m]$, of the degrees, $m = \frac{t \times 1000}{P}$, calculated for each of the successive millings, included between any two removals of samples.

With removal of sample n, the total degree of mastication is equal to:

$$M_n = m_1 + m_2 + \ldots + m_{n-1} + m_n$$

or, as has already been calculated for the preceding removal of sample number $n-1$, the sum equals

$$M_{n-1} = m_1 + m_2 + \ldots + m_{n-1}$$
$$\text{giving } M_n = M_{n-1} + m_n$$

Other experiments were made at different times but they did not furnish such complete results as those in Tables II and III.

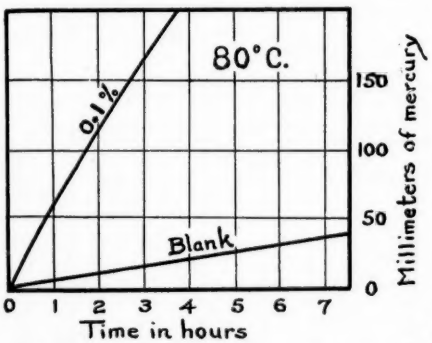

Figure 13—Influence of 0.1 Per Cent of Iron, in the Form of Its Acetylacetonate, Introduced by Milling before Vulcanization (3.5 Hours at 3.5 Kilograms' Pressure)

NOTE: For the sake of comparison with Fig. 14, the scales of the abscissas are not the same on the two diagrams; they have been chosen in such a way as to render the control samples superposable.

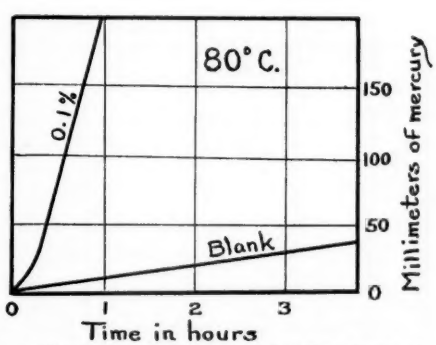

Figure 14—Influence of 0.1 Per Cent of Iron, in the Form of Its Acetylacetonate, Introduced by Diffusion after Vulcanization (3.5 Hours at 3.5 Kilograms' Pressure)

NOTE: For the sake of comparison with Fig. 13, the scales of the abscissas are not the same on the two diagrams; they have been chosen in such a way as to render the control samples superposable.

TABLE III

(COAGULATED JATEX)

IRON REMOVED FROM THE ROLLS BY COAGULATED JATEX DURING MILLING ON LABORATORY APPARATUS

The Iron Contents Given in This Table Are Those Shown on Fig. 1

No. of Sample	Time of Milling in Minutes	Weight of Sample before Removal	Viscosities (Time of Flow in Seconds)	Degree of Mastication	Iron Content in % (Average of 2 Expts.)
A1	2	87		22	0.013
A2	5	77	5400	61	0.10
A3	8	67	535	106	0.22
A4	11	57	67	159	0.25
A5	14	47	12.7	222	0.30
A6	17	37	6.7	303	0.47

Other experiments were made at different times but they did not furnish such complete results as those in Tables II and III.

Table IV gives the proportions of iron found in these samples of crepe masticated on the same laboratory mill.

The samples are arranged in the order of decreasing viscosities, that is to say, of increasing mechanical treatment.

TABLE IV

(VARIOUS SAMPLES OF CREPE)

IRON REMOVED FROM THE ROLLS BY VARIOUS SAMPLES OF CREPE DURING MILLING ON A LABORATORY MILL

No. of Sample	Viscosities (Time of Flow in Seconds)	Iron Contents in Per Cent
G1	7200	0.008
AR1	112	0.014
M8	12	0.016
G10	7.4	0.020
G12	6	0.024
AR4	3.5	0.020

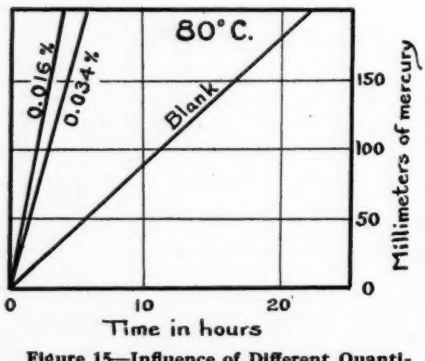

Figure 15—Influence of Different Quantities of Iron, in the Form of Its Acetylacetonate and of Ferric Chloride, Introduced by Diffusion, after Vulcanization, in a Mixture Accelerated with Diphenylguanidine (Rubber 100, Sulfur 3.5, Diphenylguanidine 1, Zinc Oxide 5), Vulcanized 1 Hour at 143° C.

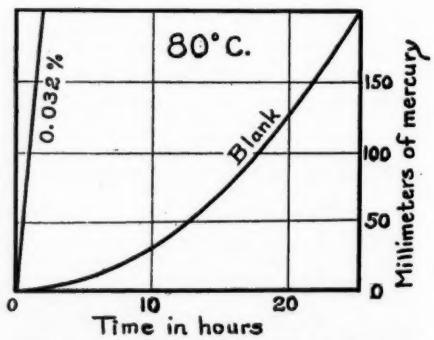

Figure 16—Influence of 0.032 Per Cent of Iron, in the Form of Its Acetylacetonate, Introduced by Diffusion, into Crepe Extracted with Acetone

Other tests were made on a large factory mixing mill. Table V gives the results of some determinations of iron in one of these experiments, where one kilogram of pale crepe was masticated for 10 minutes, with removal of samples from time to time.

A comparison of Tables IV and V shows that less iron is removed from a large roll mill than from a small one, at given viscosities.

Viscosities

In the theoretical part it was seen that, besides the degree of mastication as defined above, the viscosities of the rubber solutions were also used as a criterion of the mechanical treatment. Since comparisons only are concerned here, it was considered sufficient to give the proximate result of the measurement expressed as the time of flow in seconds of a solution of 1 gram of rubber in 25 cubic centimeters of benzene between two marks of a pipette, which were always the same, at a constant temperature of 20° C.

The pipette comprised a cylinder 13 millimeters in internal diameter and 30 millimeters long, which was extended at the lower part by a capillary 2.2 millimeters in internal diameter and 150 millimeters long. The upper part ended in a tube 5 millimeters in diameter carrying the initial reference mark; the second mark was

TABLE V

INTRODUCTION OF IRON INTO THE CREPE BY MILLING ON A LARGE FACTORY MIXING MILL

No. of Sample	Time of Milling (Minutes)	Viscosities (Time of Flow in Seconds)	Iron Content in Per Cent
Crepe (control)	0	∞	0.002
XA 1	1	7200	0.0036
XA 4	6	34	0.007
XA 7	10	11	0.012

on the capillary 58 millimeters from the first. The volume between the two marks corresponded to a mass of water of 5.254 grams at 20° C.

Investigation of the Form of Iron

A 300-gram sample obtained by milling for 53 minutes, which was reported in

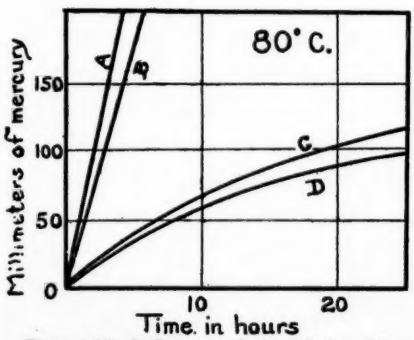

Figure 17—Influence of the Mode of Introduction of 0.1 Per Cent of Iron, in the Form of Its Acetylacetonate, on the Oxidizability of a Mixture of Crepe with 6 Per Cent Sulfur, Both before and after Vulcanization (3.5 Hours at 3.5 Kilograms' Pressure)

Vulcanized	A	Introduction by milling
	B	Introduction by diffusion before milling
Raw	C	Introduction by milling
	D	Introduction by diffusion before milling

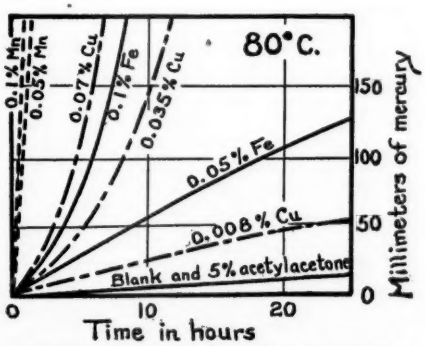

Figure 18—Comparison of the Effects of Different Proportions of Iron (Solid Lines), of Copper (Dot-Dash Lines) and of Manganese (Dotted Lines), in the Form of Their Acetylacetonates, Introduced by Diffusion, on the Oxidizability of Raw Crepe

Table II, was dissolved in a 3-liter flask with 2.5 liters of benzene. After several days of periodic stirring the liquid was left in darkness for two months to allow it to settle. At the end of this time it was decanted off by a siphon. The residue which was a gluey, black substance at the bottom of the flask, was taken up in benzene, decanted again, washed with hot benzene, then with ether, and finally dried. A black powder weighing 0.84 gram was obtained.

The decanted liquid, which was colloidal and dichromatic, still held some iron in suspension. It was centrifuged in 60 cubic centimeter fractions at 5000 revolutions per minute for 1 hour in three stages to minimize overheating. After washing and drying 0.228 gram of black powder was obtained.

The liquid obtained in this way was still dichromatic. Part of it was then removed and centrifuged at 8000 revolutions per minute for a total of 48 hours, and this time a clear yellow liquid was obtained, which showed only a feeble Tyndall phenomenon.

Determination of Iron in the Solution Centrifuged 48 Hours

After evaporation and incineration, a determination of the iron by the ordinary colorimetric method gave 0.03 per cent, based on the weight of dry rubber. This content represented about one-fifth of the total iron.

Determination of Iron in the Solid Product Obtained by Precipitation

The original sample weighed 300 grams, and contained 0.15 per cent of iron, making 0.45 gram of the metal. In the centrifuged solution the mass still contained 0.03 per cent, or 0.09 gram, or a total weight of deposited iron equal to $0.45 - 0.09 = 0.36$ gram of iron. The precipitate weighed $0.84 + 0.22$ gram, or 1.06 grams of black powder, the iron percentage of which should theoretically have been:

$$\frac{0.36}{1.06} \times 100 = 34\%.$$

Volumetric determinations, based on the hydrogen evolved, were unsuccessful, since the powder was not attacked by cold hydrochloric acid. This proved the absence of metallic iron.

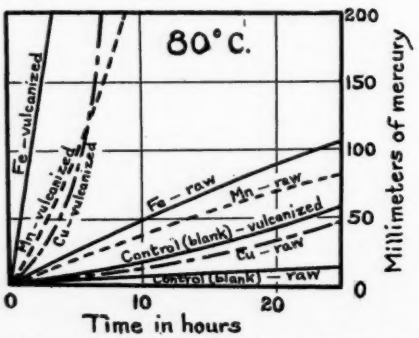

Figure 19—Comparison of the Effects of 0.1 Per Cent of Iron (Solid Lines), of Copper (Dot-Dash Lines) and of Manganese (Dotted Lines), in the Form of the Acetylacetonates, Introduced by Milling, on the Oxidizability of a Mixture of Crepe with 6 Per Cent Sulfur, Both before and after Vulcanization (3.5 Hours at 3.5 Kilograms' Pressure)

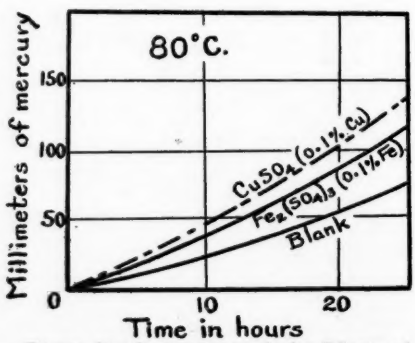

Figure 20—Comparison of the Effects of 0.1 Per Cent of Iron and of Copper, in the Form of Their Sulfates, and Introduced by Milling, on the Oxidizability of a Mixture of Crepe with 6 Per Cent Sulfur, Vulcanized 3.5 Hours at 3.5 Kilograms' Pressure

Twelve milligrams of powder were then dissolved completely in hot solution and the metal was determined colorimetrically by the usual method. The quantity found was 38 per cent.

A new determination, carried out this time on the ash from 24 milligrams of powder, gave 43 per cent of metal. In view of the marked heterogeneity of the deposit studied, the agreement between the two determinations was satisfactory. The loss of weight by incineration was 38 per cent, and this corresponded to the organic part of the deposit.

The powder obtained by decantation must have contained therefore approximately 40 per cent of iron and 40 per cent of organic matter.

The 20 per cent of unidentified residue might correspond in part to inorganic substances, and in part to oxygen combined with the iron in the form of oxide, since in the calculations the metal was assumed to be in the free state.

Introduction by Diffusion

The different acetylacetonates were generally introduced into the rubber by diffusion of their ether or chloroform solutions.

The method involves immersion of the rubber sample for a predetermined time in a graduated cylinder containing the titrated solution of salt. The volume of solution absorbed is calculated from the levels of the liquid before and after immersion, and from this the weight of acetylacetonate introduced is calculated. One gram of a thin film of crepe absorbed approximately 5 cc. of ether in 3 minutes, with a possible error of the order of 0.5 cc., *i. e.*, a precision of 10 per cent.

In the case of vulcanized rubber, the absorption was too slight to be determined by measuring the volume. It was therefore determined gravimetrically. The solution was placed in a tube of large diameter closed by a stopper through which passed tightly a rod, at the end of which a hook was suspended.

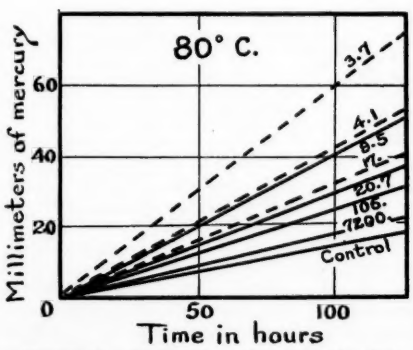

Figure 21—Comparison between the Oxidizability of Samples of Raw Crepe Mixed on Wooden Rolls (Solid Lines) and on Steel Rolls (Dotted Lines) Taking into Account the Coefficients of Mastication Represented by the Viscosities Expressed as Times of Flow (in Seconds) in a Pipette

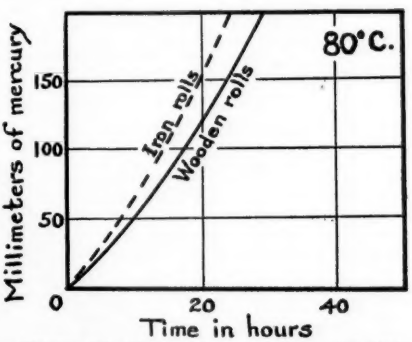

Figure 22—Comparison between the Oxidizability of Two Samples of a Mixture of Rubber with 6 Per Cent Sulfur, Vulcanized 3.5 Hours at 3.5 Kilograms' Pressure, One Sample Being Mixed on Wooden Rolls, the Other Sample on Steel Rolls, and Each Subjected to Practically the Same Milling Treatment. At the End of the Milling, the Viscosities Were 9.8 Seconds for the Sample Milled on Steel Rolls and 14 Seconds for That Milled on Wooden Rolls, Each Expressed as Times of Flow in a Pipette

The tube, solution, stopper, rod, and hook were weighed, after which a one-gram sample of rubber was suspended on the hook. The rubber was then immersed in the liquid for a definite time, after which without opening the tube the rod was raised so that the excess liquid could drop into the free space, without allowing it to evaporate. The rubber sample was then removed, whereupon a new weighing of the tube gave the weight of solvent which had penetrated into the rubber.

One gram of vulcanized rubber absorbed approximately 0.25 gram of ether in 2 minutes.

As was pointed out in the theoretical part of the work, immersion in the pure solvent increased only slightly the oxidizability (see Fig. 9 in particular), so that it was not considered necessary in the majority of cases to immerse a control sample.

After immersion, the samples were placed in a vacuum for 24 hours to eliminate completely the solvent which might cause trouble in the manometric measurements of absorption.

In order to introduce any desired quantity of metal, a preliminary measurement

of the volume or the weight of pure solvent absorbed in a given time by an identical rubber sample was made, and from this value was calculated the necessary concentration of metal in the solution.

Experimental Technic of the Oxidation

The usual technic of the authors was employed. This involved enclosing one gram of substance in small vessels, all of the same capacity, each connected with a manometric tube. A certain number of these vessels were connected with one another by the lower end of their manometric tube, which made it possible to treat a series of samples simultaneously and in an identical way, to expel the gas in a high and controlled vacuum (0.01 mm.), to fill the vessels with oxygen, to carry out the heating, etc. In this way the most closely comparable conditions were attained.

According to the usual practice of the authors, the curves in the diagrams are not based upon the quantities of oxygen absorbed but upon the manometric

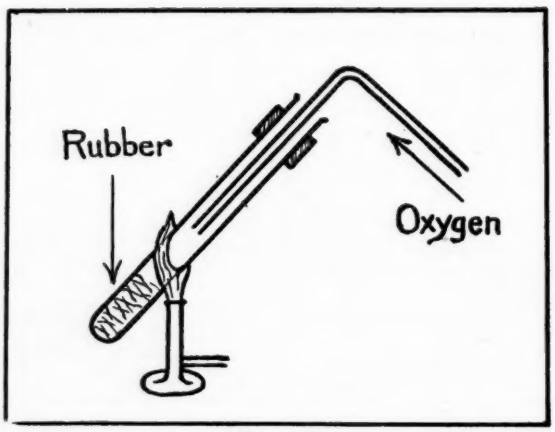

Figure 23

readings. Both values express equally well the course of the absorption of oxygen, and the second method is preferable because it avoids unnecessary calculations.

A further simplification is to have in each experiment a control vessel, identical to the others and containing only oxygen. The level of the mercury in the manometer of this control serves as a zero reading for measuring the heights of the mercury columns in the other vessels. In this way it becomes unnecessary, for satisfactory approximate results, to correct each reading for the changes in temperature and external pressure.

All of the oxidations were carried out in a thermostat at 80° C. controlled to ±2° C. The initial pressure of oxygen in the apparatus was in all cases approximately standard.

For reasons already discussed in earlier papers,[21, 22, 23] the tests cover only the beginning of oxidation, *i. e.*, the only stage of oxidation which gives useful information about the behavior of rubber. In view of this, the capacity of the vessels was calculated so that their supply of oxygen would not exceed one per cent of the mass to be oxidized.

References

[1] *Chem. News*, **64**, 169 (1891).
[2] *J. Soc. Chem. Ind.*, **17**, 677 (1898).
[3] *Kolloid. Z.*, **9**, 81 (1911).
[4] *Agr. Bull. St. Fed. Malay St.*, **17** (1912).
[5] *J. Soc. Chem. Ind.*, **31**, 348 (1912).
[6] *Tropenpl.*, **25**, 35, 83 (1922).
[7] *Ind. Eng. Chem.*, **17**, 866 (1925).
[8] Van Rossem and Dekker, *Ind. Eng. Chem.*, **18**, 1152 (1926).
[9] *Kautschuk*, **1927**, 256.
[10] *Ind. Eng. Chem.*, **20**, 132 (1928).
[11] *Malayan Agr. J.*, **16**, 204 (1928).
[12] *Trans. Inst. Rubber Ind.*, **4**, 374 (1929).
[13] *Compt. rend.*, **191**, 1126 (1930).
[14] Kirchhof, *Kautschuk*, **7**, 26 (1931).
[15] *Ind. Eng. Chem.*, **24**, 320 (1932); RUBBER CHEM. AND TECH., **5**, 179 (1932).
[16] *Ann.*, **498**, 129 (1932).
[17] *Kautschuk*, **9**, 34, 49 (1933); RUBBER CHEM. AND TECH., **6**, 378 (1933).
[18] *India Rubber World*, **88**, 28 (1933).
[19] *Rev. gén. caoutchouc*, **8**, No. 75, 179 (1931); RUBBER CHEM. AND TECH., **5**, 153 (1932).
[20] *Ind. Eng. Chem.*, **24**, 140 (1932); RUBBER CHEM. AND TECH., **5**, 164 (1932).
[21] Dufraisse and Drisch, *Rev. gén. caoutchouc*, **8**, No. 75, 39 (1931); RUBBER CHEM. AND TECH., **5**, 301 (1932).
[22] Dufraisse, *Rev. gén. caoutchouc*, **9**, No. 85 and 86 (1932).
[23] Dufraisse, Drisch, and D. Pradier-Gibello, *Rev. gén. caoutchouc*, **10**, No. 94 (1933); RUBBER CHEM. AND TECH., **7**, 167 (1934).

[24] Furnished by The Third Mile Rubber Co. Ltd.

[25] In the experimental section will be found a method of calculating the degree of mastication, by which such comparisons are possible.

[26] Since the control samples were not the same in the two experiments, two abscissa scales were chosen in order to have the same inclination of the curves of the control samples in the two diagrams. This facilitates a comparison of the activities.

[27] This was true with a capacity of approximately 8 cc. of oxygen and one gram of vulcanized rubber cut up coarsely with scissors.

[28] The two sets of apparatus were obtained through the coöperation of M. Leroy, mechanical engineer at the Clichy factory of the Société Industrielle des Téléphones, and we wish to show our appreciation to him for his kindness. We also wish to thank M. Iung, Président du Conseil d'Administration of the above company, as well as M. Mensier, Director of the Clichy factory, for the facilities which they kindly allowed us to use in carrying out our experiments.

[29] This latex was furnished by The Third Mile Rubber Co. Ltd. of Edinburgh, which was kind enough to undertake at our request the gathering and transporting of the latex in glass bottles with ground glass stoppers, therefore without contact with metal.

[Reprinted from Transactions of the Institution of the Rubber Industry, Vol. 9, No. 3, pages 169–187. October, 1933.]

Oil-Resisting Rubber

W. J. S. Naunton, Maldwyn Jones, and W. F. Smith

From the mechanical engineer's point of view, rubber has one serious drawback, and that is the behavior toward lubricating oil. By proper compounding and curing, rubber is being used under circumstances which involve contact with oils, but there is still room for improvement. When one considers that oil-resisting rubber is finding and could find still greater application in the engineering, especially the automobile, electrical, petroleum, gas, paint, printing, agricultural, and other industries, it is not astonishing that this problem is one of the most important of the rubber industry.

Little work, however, has been published on this subject prior to the present year. The popular belief that glue protects rubber against oil has been shown to be incorrect, and will be dealt with later in the paper.

Ishiguro (RUBBER CHEM. & TECH., **6**, 278 (1933)) studied a large number of fillers, soaps, glue, starch, and accelerators, but in view of the fact that the author did not make a preliminary study of the effect of these substances upon cure, the reader of the paper is left with the impression that the results are due as much to the effect of the various substances upon the state of cure as to their intrinsic oil-resisting properties. It is true that a certain amount of correction was made in the case of accelerators. The paper must, however, be welcomed as the first systematic publication based on experimental work on this subject. Karsten (*Kautschuk*, **9**, 73 (1933)) brings out a very important point in his paper to the effect that the best method of obtaining oil-resistance in rubber must depend upon the use to which the finished article will be put: for example, large proportions of reinforcing fillers and glue cannot be used when a flexible rubber is required, and so on.

Hayden and Krisman (RUBBER CHEM. & TECH., **7**, 393 (1934)) have published a paper on the use of synthetic rubber and resin in the compounding of oil-resistant rubber, but in view of the fact that these products will be discussed later in this paper no comments will be offered upon these papers.

Theoretical.—How can a picture be formed of the action of oil upon rubber? It is now generally agreed that the rubber molecule can be regarded as a spiral chain or spring of *cis*-isoprene molecular units (Fikentscher and Mark, *Kautschuk*, **6**, 12 (1930)). The residual affinities between the unsaturated centers of the isoprene units are the forces which hold the spring together. Now straight (non-polar) molecules such as hydrocarbons can easily insert themselves between the coils of the spring and open up the structure (*i. e.*, swell the rubber), in fact completely break up the spring (*i. e.*, dissolve the rubber). When the rubber vulcanizes, however, the sulfur forms bridges between the coils of the spring and reinforces it or, in other words, a stronger spring is produced which is more difficult to open. Vulcanized rubber is therefore not so readily attacked by oil. Molecules (polar) with a cross-bar cannot insert themselves between the coils, and hence short polar molecules (alcohol) cannot swell rubber, but long polar molecules such as linseed oil can swell rubber, but not as readily as hydrocarbon oils which are non-polar (see Fig. 1). There are therefore three ways of solving the problem:

(1) *By Wrapping Up the Molecule, So to Speak, in an Oil-Proof Wrapping.*—Fillers which are miscible with rubber and unaffected by oil probably act in this

way, and therefore show a true protecting action, as opposed to a dilution effect. This effect should not be confused with protecting the finished article with an oil-resisting finish.

(2) *By Holding the Spring Together and Hence Resisting the Insertion of the Oil Molecules.*—This effect can be produced in three ways: (*a*) by external physical means; thus, by confining the rubber so that it cannot expand and so cannot absorb oil; (*b*) by internal physical means, such as by the use of reinforcing fillers, such as magnesium carbonate, which by surface energy effects hold the springs in a compressed state; (*c*) by chemical means, by knitting the coils of the spring together; thus the better the cure the more resistant to oil is the rubber. "Modified" rubbers are in the same way more resistant to oil.

(3) *By Not Using a Material with a Spiral Structure*, or at least using the least possible proportion of material of such structure. Thus a heavily loaded rubber is, of course, more resistant than a rubber with less filler: or the rubber can be re-

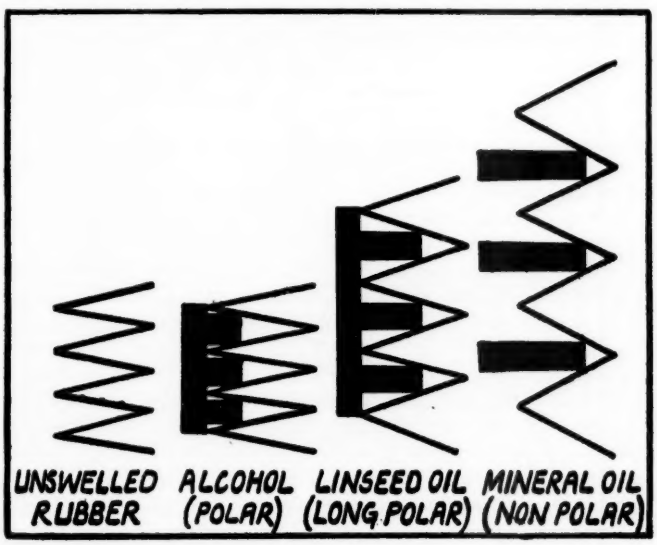

Figure 1

placed either partially or wholly by such substances as polymerized ethylene polysulfide or polymerized glycerol phthalate, which do not possess spiral structures.

Experimental Technic

(*a*) *Curing.*—With each substance examined, a preliminary study of curing conditions was made, and the effect of the substance on oil-resistance was studied in an under-cured, optimum and over-cured rubber.

(*b*) *Temperature.*—Preliminary experiments were made at 20°, 55°, and 100° C., and it was decided that the greater part of the work should be carried out at 55° C., since working at room temperature prolonged the tests and 100° C. probably gave abnormal results due to after-curing during the oil immersion. Moreover, under practical conditions the lubricating oil which came into contact with rubber accessories would probably be warmer than room temperature but not as hot as 100° C. (see Fig. 2).

(*c*) *Nature of the Oil.*—Preliminary experiments were carried out with the following oils at 55° C.; butter fat, Diesel fuel oil, linseed oil, spindle lubricating oil, and transformer oil (see Fig. 3).

Different oils have different effects upon natural and synthetic rubber, and it was therefore essential to select an oil which had a proportionally drastic action upon both types. Diesel fuel oil fulfilled this condition. Six days in Diesel oil at 55° C. was therefore selected as the routine test. A skeleton rubber mix (*i. e.*, diphenylguanidine, zinc oxide, and sulfur) in the form of a Schopper disc under these conditions takes up 290 grams of oil for each 100 grams of rubber, and this

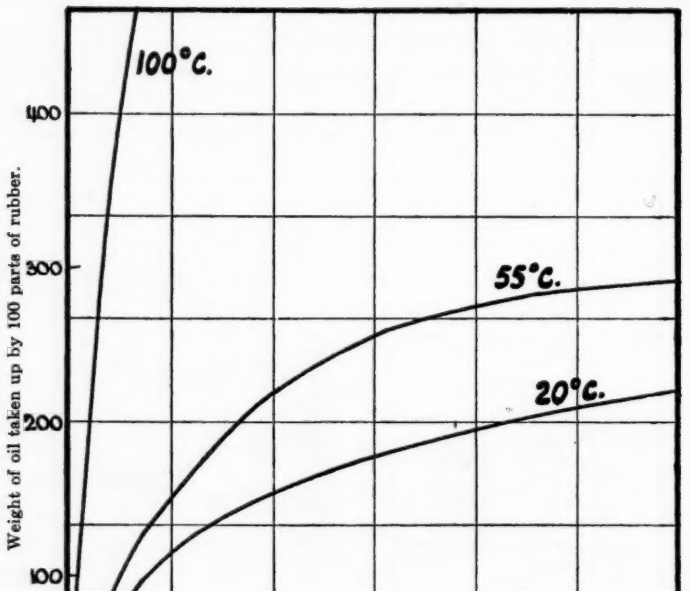

Figure 2—Effect of Temperature on Oil-Resistance

figure is taken as the standard in this work. Rubber takes up about one-half this quantity of linseed oil or butter fat, and intermediate quantities of transformer and spindle oil under similar conditions.

When the new synthetic rubber Duprene is considered it is found that Diesel oil is still the most drastic, but the other oils are arranged in quite a different order, for example, there is a considerable difference between linseed oil and butter fat, and transformer oil has the least effect (see Fig. 4).

(*d*) *Exposure to the Oil.*—Discs from the centers of Schopper rings which had been used in the physical study of curing conditions were suspended in the oil in a Hearson thermostatically controlled oven. These discs were periodically wiped

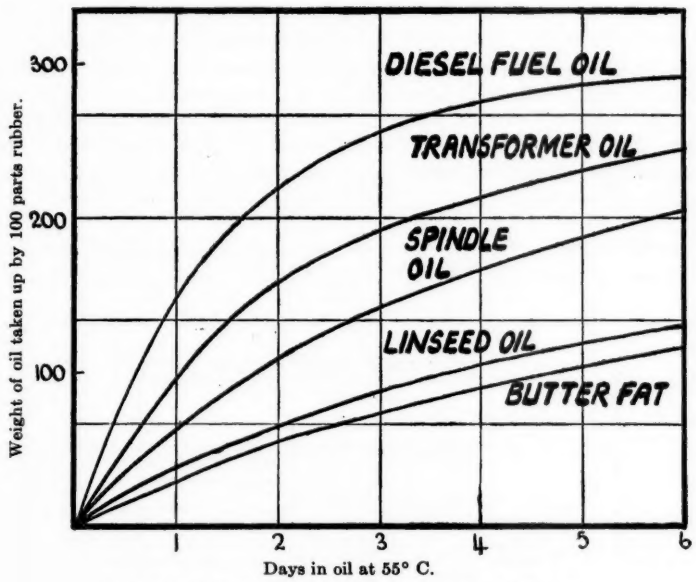

Figure 3—Effect of Different Types of Oil on Rubber

and then measured and weighed. In all cases the physical state of the rubber was noted and where reasonable physical properties had been retained the tests were repeated with Schopper rings, which after immersion were broken in the tensile machine.

(*e*) *Representing the Results.*—For some purposes such as representing the effect of cure upon the oil-resistance of a simple rubber-sulfur mix it is sufficient to plot the increase in weight against the time of immersion, but for the study of the effect of compounding ingredients it is better to plot the weight of oil taken up by a unit weight of rubber in the compound, since by this means it is possible to find out if the particular ingredient is actually protecting the rubber or merely exerting a diluting effect.

The more important factors influencing the oil-resistance of rubber are as follows:

Nature of the Rubber.—Overmilling definitely lowers the oil-resistance of rubber; hence it was thought that rubber produced directly from latex without milling should exhibit better oil-resistance. This was found to be the case, and further-

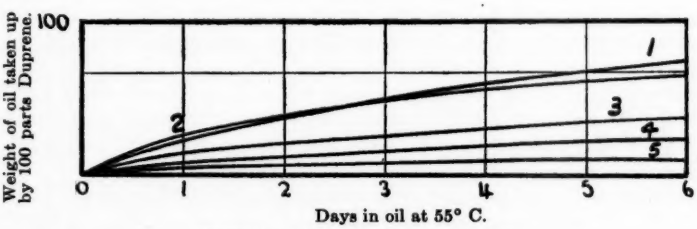

Figure 4—Effect of Oils on Duprene

1. Linseed oil. 2. Diesel oil. 3. Spindle oil. 4. Butter fat. 5. Transformer oil

more it was shown that milling a mix made by the drying of compounded latex reduced the oil-resistance to that of a similar compound made from dry rubber. These results led to the idea that it might therefore be more effective to protect the rubber in latex form with the usual protective agents. The following substances were found to exert a protective action, and though the differences between their respective effects were comparatively small, the following is the order found under the particular conditions: methylcellulose (patent applied for), casein, glue, gelatin, water-soluble glyptal resin, untreated latex rubber, and latex mix containing glue but dry milled.

It will be seen (Fig. 5) that if the latex compound containing glue be milled after drying (either by spraying or drying in sheet form), the oil-resistance is actually

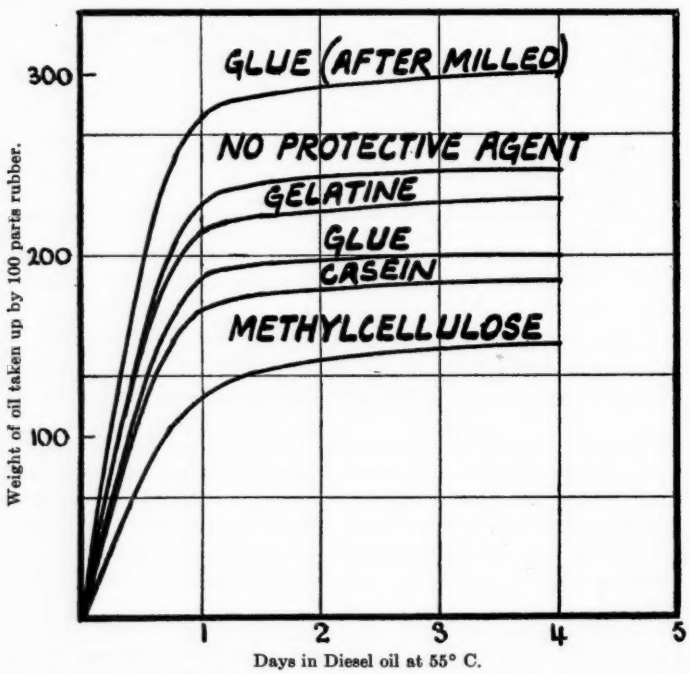

Figure 5—Effect of Protective Agents on Resistance of Latex-Compounded Rubber

less than that of an unmilled latex rubber made without milling. The discs used in this work were one-half the usual thickness of Schopper discs; hence the difference in the slope of the absorption curves.

When glue is used in the way described above, it does actually exert a protective effect upon the rubber, which is interesting in view of the fact that it has been impossible to find any indication of protective action by glue when milled into a dry rubber mix.

Effect of Cure.—There is a more or less general belief that the longer the cure the greater is the oil-resistance, and that one must make a compromise between the long cure necessary for oil-resistance and the reasonable cure essential for good aging. This is only true under certain conditions. The authors therefore set out

to study a long series of cures, ranging from under-cured soft rubber up to ebonite, to find if oil-resistance could be correlated with any well-known physical property such as tensile strength. In the early experiments conducted with a typical diphenylguanidine-accelerated soft rubber mix, it was shown that the oil-resistance curve followed (but was displaced to the right) the tensile strength curve (see Fig. 6).

When, however, the experiments were repeated but with a diphenylguanidine-accelerated mix sufficiently rich in sulfur to be carried through to a hard rubber,

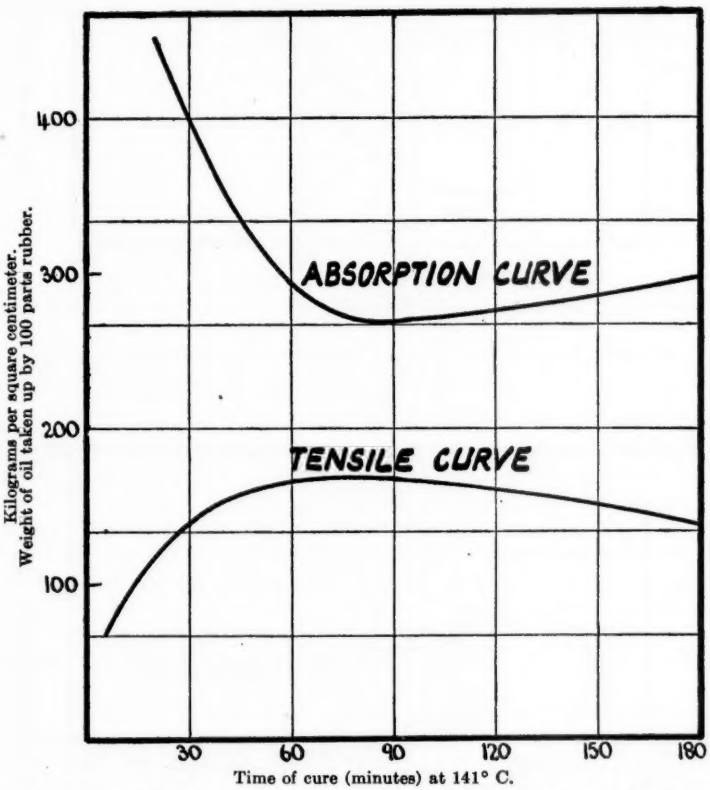

Figure 6—Effect of Cure on Oil-Resistance After Six Days in Diesel Oil at 55° C.

it was found that the oil-resistance did not follow the tensile curve but steadily improved up to the hard rubber stage; in other words, it more or less followed the Shore hardness curve (see Fig. 7). Further series of tests conducted with intermediate proportions of sulfur showed that the cause of the falling-off of the oil-resistance was due to reversion of the rubber. It is for the same reason that the oil-resistance of rubber cured with tetramethylthiuram disulfide without sulfur is maintained through gross over-cures, whereas that of rubber cured with the same accelerator with sulfur falls off with prolonged over-cure.

Rubber cured with TNB (trinitrobenzene) is more oil-resistant than sulfur-cured rubber (see Fig. 8). Here again the full oil-resistance is only developed after

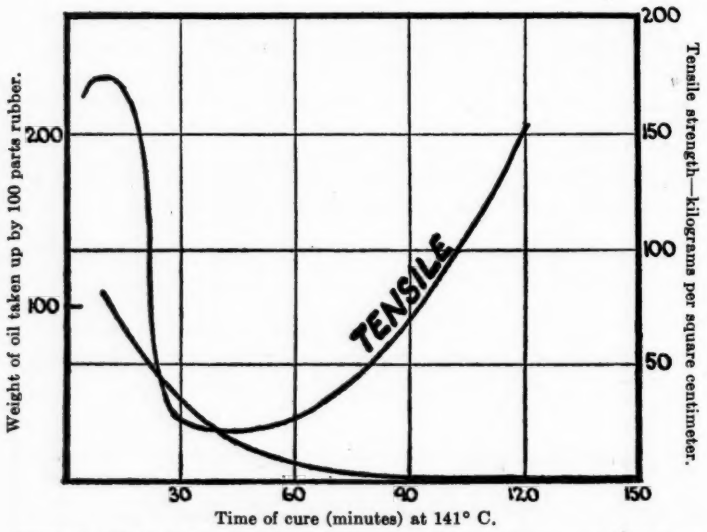

Figure 7—Effect of Cure on Oil-Resistance of Ebonite Compound after Four Days in Spindle Oil at 55° C.

the optimum cure, in fact there is a fairly rapid increase in oil-resistance up to about 100 per cent over-cure. The mix employed in the experiments was rubber, 100 parts; gas black, 90 parts; and trinitrobenzene 4 parts.

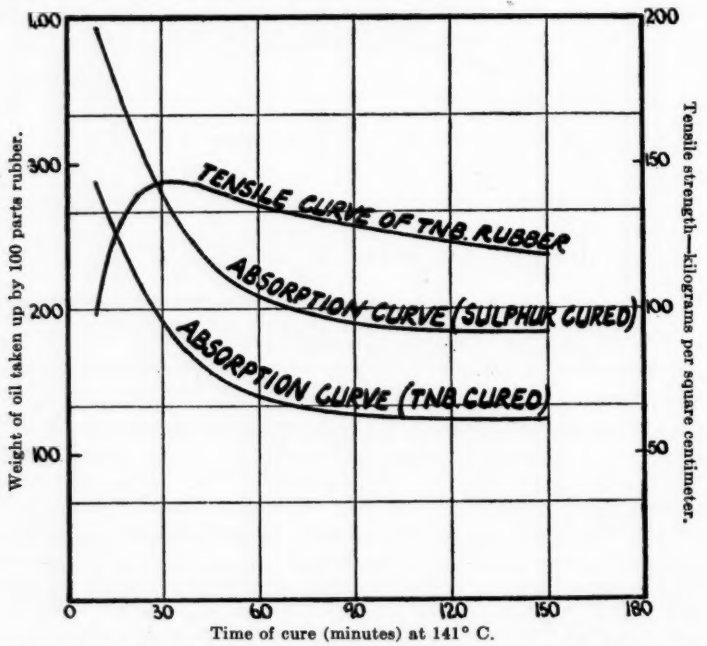

Figure 8—Oil Absorption of TNB-Cured Rubber after Four Days in Diesel Oil at 55° C.

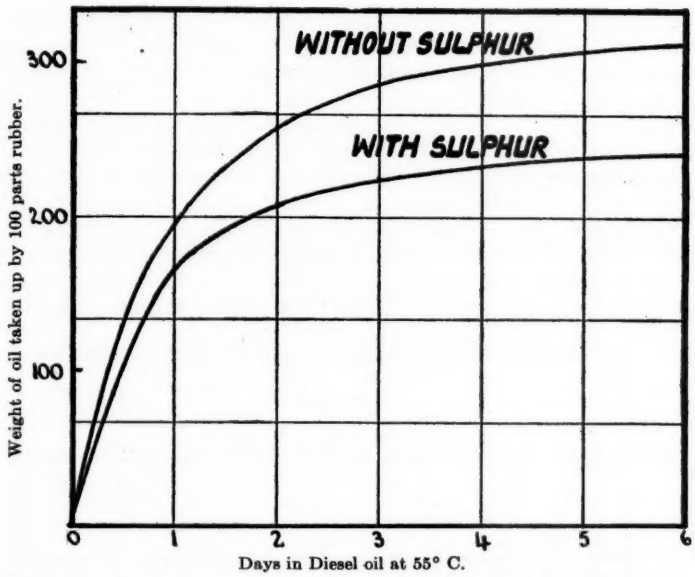

Figure 9—Oil Absorptions of Rubber Cured with TMT with and without Sulfur

Effect of Accelerators.—In view of the remarkable effect which accelerators have upon the general physical properties of rubber compounds, their action in connection with the oil-resisting properties of rubber is at first disappointing. A well-cured (four to six hours at 40 lbs.) non-accelerated mix takes up no more oil than an accelerated compound of high tensile strength, but there is a difference and an important difference, and that is, that although the non-accelerated mix takes up less oil, its tensile strength and general physical properties after swelling in oil are below those of the accelerated mix. Generally speaking there is little difference in effect between accelerators when the accelerated compounds are examined at, or slightly over, their optimum cures.

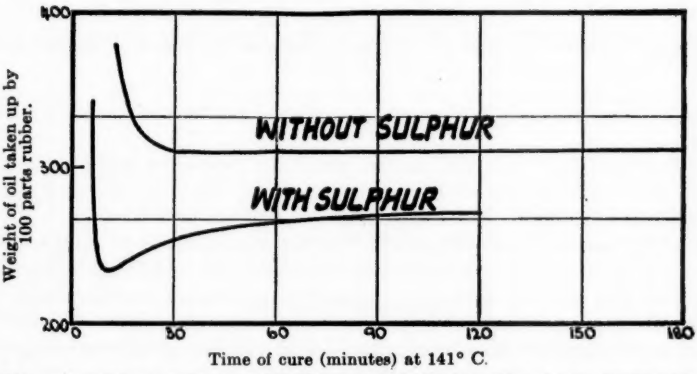

Figure 10—Effect of Cure on Oil Absorption of Rubber Cured with TMT with and without Sulfur

Rubber cured with tetramethylthiuram disulfide alone or with very little sulfur takes up more oil than one cured with the same accelerator with the usual proportion of sulfur (Fig. 9), but retains its tensile strength slightly better after swelling, and its oil-resistance is less affected by over-cure (Fig. 10).

Effect of Different Fillers.—Fifty volumes of filler were added to that weight of skeleton mix (rubber, diphenylguanidine, zinc oxide, and sulfur) which contained 100 volumes of rubber, and discs cured under optimum conditions were examined.

For obvious reasons a filled rubber swells less than an unloaded mix, since most fillers are unaffected by oil and exert a diluting effect upon the rubber. With most fillers there is a slight protective action, which in the case of magnesium carbonate seems to be of appreciable magnitude. Furthermore, fillers cause the swelled rubber to retain its tensile strength longer than unfilled rubber. Gas black does

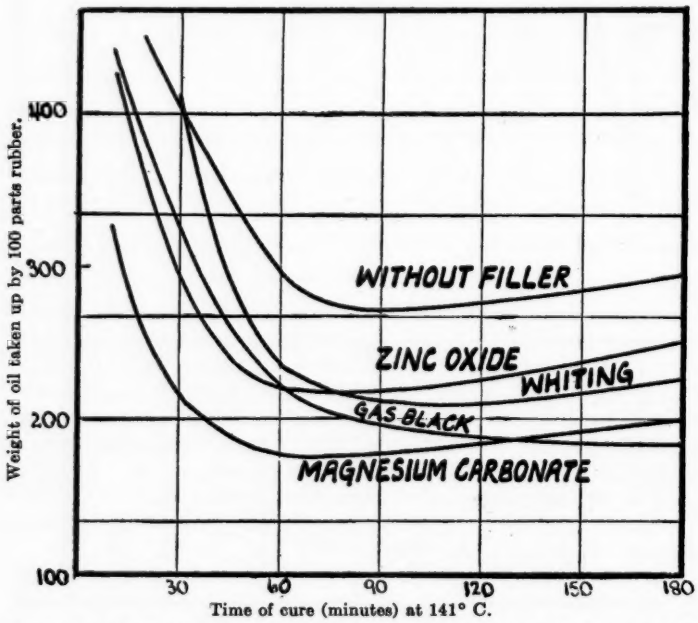

Figure 11—Effect of Fillers on Oil Absorption after Six Days in Diesel Oil at 55° C.

not give the same protective action when employed in a non-milled latex compound (see Fig. 11).

In rubber cured with trinitrobenzene, gas black shows a greater protective action than zinc oxide, in fact the difference is greater than any shown by different fillers in sulfur-cured rubber (see Fig. 12).

Effect of Softeners.—Most softeners reduce the oil-resistance of rubber, probably because they are themselves usually either miscible with or soluble in oil.

Thus pine tar, zinc stearate, zinc palmitate, aluminum stearate, and soluble and insoluble soaps generally (except where they are used under such conditions as to act as accelerators of vulcanization), dark substitute, mineral oils, paraffin wax, petrolatum, naphthalene, coumarone resins, and chlorinated naphthalene waxes (it is interesting to note here that the higher the degree of chlorination of

the wax the less harmful its effect upon oil-resistance), all lower the oil-resistance of rubber.

Glue and Vulcatac S. (a special soft heat-cured substitute made from a gas-treated oil) showed neither protective nor harmful action and hence are suitable softeners for use in oil-resisting rubber. In view of the fact that Vulcatac S. is much softer than ordinary dark substitute this result was surprising, though the explanation may lie in the fact that in the manufacture of Vulcatac S. the oil undergoes polymerization during the gas treatment before vulcanization.

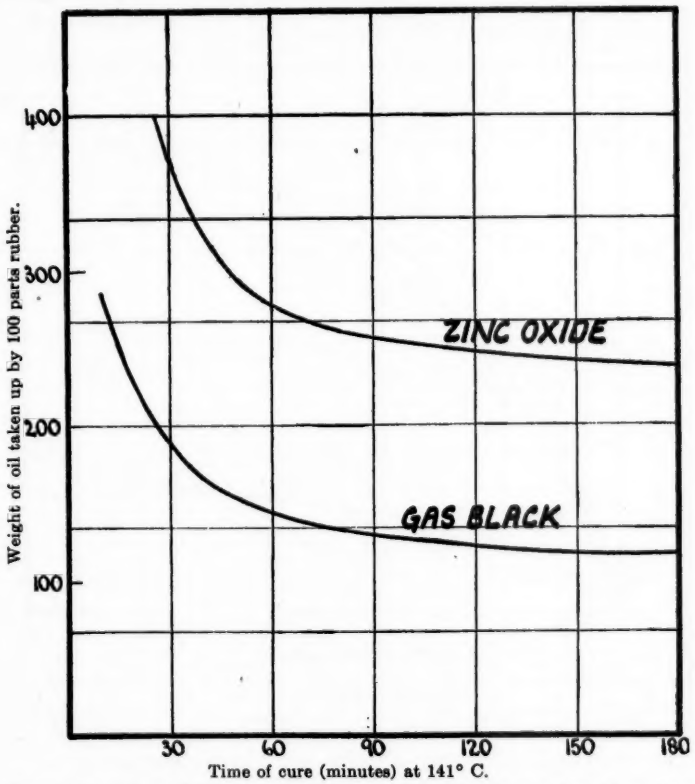

Figure 12—Effect of Fillers on Oil Absorption of TNB-Cured Rubber after Four Days in Diesel Oil at 55° C.

Although Ishiguro (*loc. cit.*) stated that glue showed no protective action, it has been suggested that his result might be due to under-cure brought about by acidity in the glue. Steps were therefore taken to employ a suitable glue and tests were made throughout a range of cures which would assure even over-cured samples, and in no case was there any indication of protective action.

Surface Treatment

Before passing on to synthetic resins and synthetic rubber, a few words should be said about the protection of rubber by surface treatment. The only satisfactory solution to this method would be to coat the rubber with a layer of oil-resisting

synthetic rubber of similar elastic properties to those of the rubber compound itself.

Apart from the use of a suitable synthetic rubber, the protection of a soft rubber by means of a suitable protective coating is difficult, since few coating media have sufficiently elastic properties. Several flexible varnishes containing drying oils were tested, but usually after about three days in Diesel oil at 55° C. the varnish coating peeled off. Flexible thermo-hardening varnishes were reasonably satisfactory provided the discs were not repeatedly flexed.

Six minutes' immersion of the disc in bromine water also gave good results, since the increase in weight of the disc after six days' immersion in Diesel oil at 55°

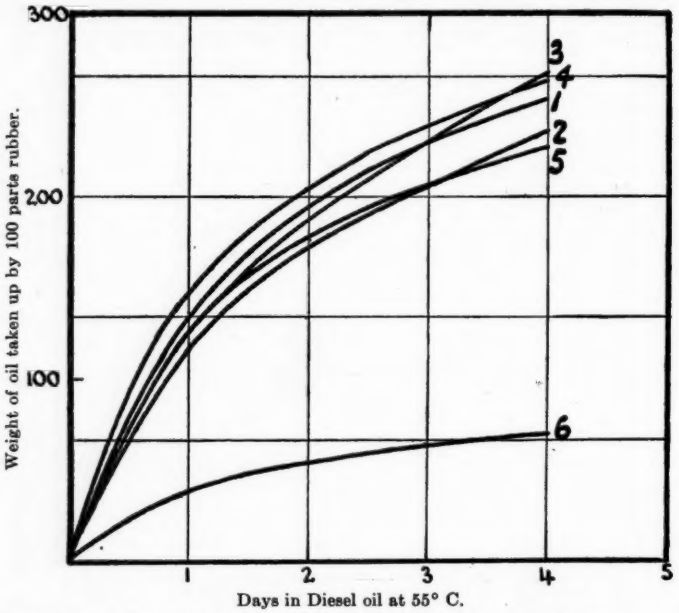

Figure 13—Effect of Ethylene Polysulfide Resin on Oil Absorption of Rubber (Optimum Cures)

1. Rubber. 2. EPR.75/R25. 3. EPR.50/R50. 4. EPR.25/R75. 5. EPR.5/R95. 6. EPR.83/R17

C. was less than the original weight of the disc. Treatment with bromine water is well known, and is satisfactory with a non-flexed rubber such as the rubber lining of chemical vessels, but the resulting hardening of the surface makes it poor protection when the rubber is stretched or abraded.

Synthetic Resins

For the successful employment of a resin in oil-resisting rubber, the resin must fulfil certain requirements: (1) It must be reasonably insoluble in oil, (2) it must be reasonably miscible with rubber, and (3) it must have little or no effect upon vulcanization.

Coumarone resins fail because of their solubility in oil. Phenolformaldehyde resins fail because of their immiscibility with rubber and their retarding effect upon vulcanization. Alkyd resins made by the condensation of polybasic acids

with polyhydric alcohols can be used under special conditions, *i. e.*, by mixing water soluble resins of low acid value with latex or by milling special plastic glyptals into rubber. The protection obtained varied from good to bad according to the skill exercised in the selection of the particular alkyd resin and the compounding and curing of the mixture. For good protection a large proportion of plastic glyptal is usually necessary.

Chlorinated rubber is to a large extent unaffected by oils, and can be compounded into rubber by mixing a dispersion with latex, or by the use of a common plasticizer such as chlorinated naphthalene, but it gives little or no oil-resistance, probably because it is immiscible with rubber and acts merely as a filler.

The resin obtained by the action of ethylene chloride upon calcium polysulfide is effective in conferring oil-resistance upon rubber when the concentration of resin is high (see Fig. 13). It is itself completely insoluble in oil, is reasonably miscible

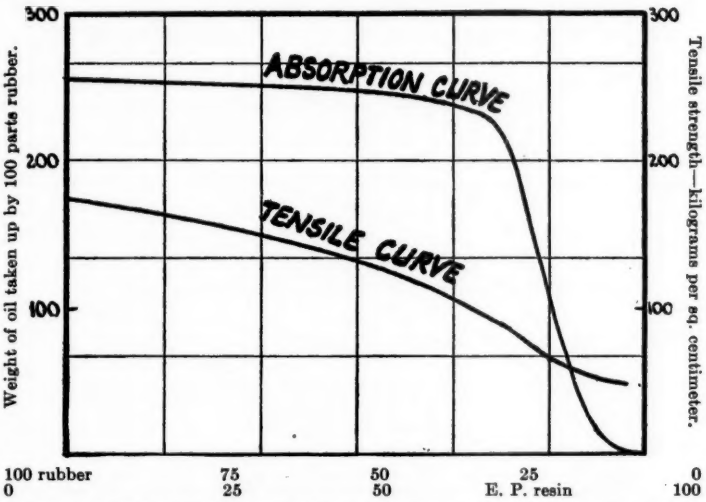

Figure 14—Effect of Ethylene Polysulfide Resin on Tensile Strength before Immersion and Oil-Absorption of Rubber. (Four Days in Diesel Oil at 55° C.)

with rubber, and does not retard vulcanization. It has unfortunately an evil smell, and when warm gives off fumes which make handling it exceedingly unpleasant. It lowers the tensile strength (Fig. 14) and general physical properties of the rubber compound into which it is introduced, and increases the oil-resistance only slightly unless used in concentrations of over 75 per cent on the rubber-resin mixture.

Plastic substitutes for rubber may now be considered in the manufacture of oil-resisting goods. They are: (1) various types of hardened gelatin, but their use is largely restricted to the manufacture of soft articles, such as lithographic rollers; (2) plastic alkyd resins made by plasticizing C-stage resins with B-stage resins, which are being employed to some extent at the present time. The degree of plasticity, which varies from very soft for printers' rollers to tough for gaskets, depends upon suitable choice of polyhydric alcohol and polybasic acid. For example, the resin obtained from glycerol and phthalic acid is brittle and thermo-hardening, whereas that from ethylene glycol and adipic acid is soft and flexible and non-thermo-hardening. Mixed resins, therefore, exhibit degrees of hardness depending

upon the proportions of the hard and soft resins; thus a lithographic roll may consist of a 1 to 10 mixture of glycerol phthalate and glycol adipate resin. Their oil-resistance is good but their manufacture takes a very long time and their aging characteristics have still to be demonstrated; (3) the ethylene polysulfide resins which have good oil-resisting properties but suffer from two serious defects, namely, obnoxious smell and thermoplasticity. The hardness range is also limited. These synthetic resins can only be molded in a mold capable of being cooled before opening, and the finished product must be one employed at moderate temperatures and not calling for good tensile strength or elongation.

Both the glyptals and polysulfide resins are probably improved by the use of a small proportion of rubber, but the finished article cannot be regarded in any way as being made of rubber.

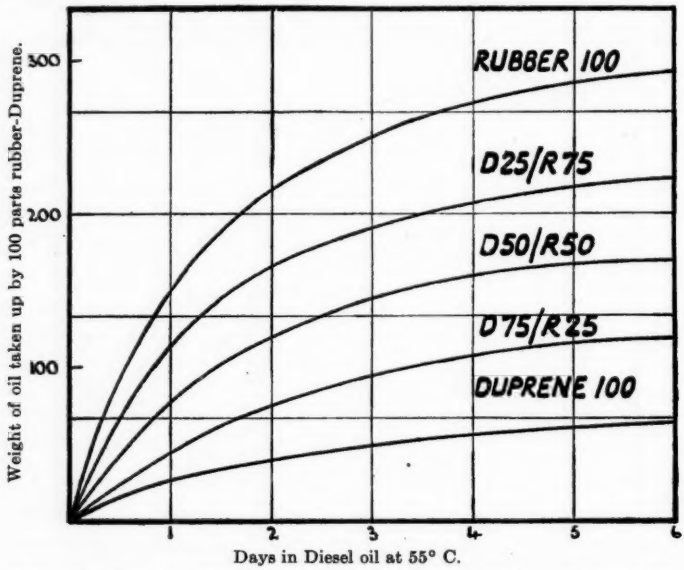

Figure 15—Effect of Duprene on Oil Absorption of Rubber-Duprene Mixtures

Synthetic Rubbers

It is exceedingly doubtful if synthetic rubber will ever replace to any extent natural rubber, and furthermore such a procedure would be economically unsound, since why should secondary energy be wasted in doing something which the plant can do far more efficiently with primary energy? Special purposes synthetic rubbers may, however, be developed and justify their existence. A good example of such a development is the new synthetic rubber Duprene developed by the du Pont Company, and which is the alpha-polymer of chloroprene. There is little doubt that Duprene represents one of the finest and most interesting technical achievements of our times. It has the toughness of the best natural rubber, but what is more interesting is the fact that it has the molecular physical structure as opposed to the chemical composition of rubber. Chemically it may be regarded as rubber in which a methyl group has been replaced by a chlorine atom, but when examined by x-rays it behaves like rubber and gives the typical diffraction pattern when stretched. It may be that its far greater resistance to oil is connected with

the increased residual affinity in the chloroprene complex, which affinity holds together the spiral structure with greater force and hence resists the intrusion of the oil molecules. The early samples of Duprene possessed a characteristic unpleasant but not distressing smell, due to the presence of an impurity, but it is now possible to produce this substance with little permanent smell.

It can be compounded either alone or with rubber in exactly the same way as rubber, and hence can be made to give products with almost any range of hardness. It cannot be over-milled. It can be vulcanized in the same way as rubber, either by the action of heat alone or by the use of sulfur. The final product is remarkably heat-resistant, since Duprene does not undergo reversion.

Duprene took up 60 grams of Diesel oil compared with the 290 grams of the same oil taken up by rubber, when exposed side by side for 6 days at 55° C. (Fig. 15). Its resistance to oil is therefore about five times better than that of rubber, but is not as good as those of ethylene polysulfide or glyptal resins. Though Duprene takes up this amount of oil, it retains to a remarkable degree its physical properties after swelling.

Duprene cannot be cured up to an ebonite, and use can therefore be made of this property to prepare an exceedingly interesting oil-resisting product, namely flexible "ebonite" (patent applied for). Since rubber cured to the ebonite stage is completely oil-resisting, a mixture of uncured ebonite mix and Duprene will, on curing, give a flexible ebonite which has excellent oil-resisting and physical properties and satisfactory aging characteristics. To illustrate this, a product may be made from a mixture of equal parts of rubber and Duprene and sufficient sulfur to take the rubber to the hard rubber or ebonite stage. This product will be flexible, and so oil-resistant that it will show practically no increase in weight when immersed in Diesel oil for 6 days at 55° C.

In conclusion the outstanding conditions in designing an oil-proof rubber may be stated thus:

(1) The rubber should be preferably unmilled (*i. e.*, latex compounded) or, if essential, the milling should be kept down to the minimum.

(2) Oils open up the structure of rubber and therefore accelerate oxidation; hence an antioxidant should always be employed in oil-resisting rubber compounds.

(3) The rubber should be cured with a liberal amount of sulfur, as apart from blooming there is no objection to the presence of free sulfur, or if cured by means of an accelerator, a thiuram accelerator should be employed.

(4) The cure should be continued as far as aging requirements and the danger of reversion will allow.

(5) The softener should be one which has no deleterious effect upon oil-resistance. Glue and Vulcatac S. are the most suitable for most purposes.

(6) The filler should be essentially magnesium carbonate, in quantity as much as the nature of the finished article will allow.

(7) Where the article will not be called upon to give service at low or higher temperatures and not to possess high grade physical properties (tensile strength and extension), the oil-resistance can be increased by the use of a large proportion of ethylene polysulfide resins.

(8) Where the finished article will be called upon to give service at higher temperatures, such as hot gaskets, the best results will be obtained by using Duprene.

(9) Where extreme resistance to oil combined with high grade physical properties are required, the best combination would be a mixture of Duprene with an ethylene polysulfide resin.

In conclusion the authors wish to express their thanks to Imperial Chemical Industries Limited for permission to publish the results embodied in this paper.

[Reprinted from Physics, Vol. 4, No. 6, pages 225–235, June, 1933.]

The Plastic Properties of Several Types of Unvulcanized Rubber Stocks at High Rates of Shear

J. H. Dillon and N. Johnston

Research Laboratory, Physics Division, Firestone Tire and Rubber Company, Akron, Ohio

An extrusion plastometer operating at rates of shear comparable with those existing in rubber tubing machines (10 to 1000 sec.$^{-1}$) is described. The relation between efflux rate and pressure at constant temperature for various types of rubber stocks was determined. For highly compounded rubber stocks, such as tread stocks, the efflux rate *vs.* pressure curves attain linearity at low rates of shear. Both the slope of the curves and the extrapolated pressure intercept vary rapidly with the temperature, indicating that both the mobility and the yield stress are functions of temperature for highly compounded stocks. For lightly compounded stocks and for crude rubber, the curves are of the power function type at the lower rates of shear, but appear to attain linearity at the very high rates. These linear portions of the curves, for a given stock at different temperatures, are approximately parallel. Elastic recovery was determined as a function of rate of efflux. The slope of the recovery *vs.* efflux rate curves decreases with increasing rates of efflux. The relation between efflux rate at constant temperature and pressure, and time of milling, is approximately linear. The extrusion plastometer is shown to be more sensitive to overmilling than is the Williams plastometer. The partial failure of the compression-type plastometer to correlate with the factory extrusion machine is explained on the basis of the much lower rates of shear employed in the compression-type instrument than those existing in the extrusion machine.

Introduction

Marzetti,[1,2,3] Griffiths,[4] and others[5,6,7] have employed the extrusion method for studying the plastic properties of unvulcanized rubber. Some of the results, particularly those of Marzetti, have been very interesting from an academic standpoint. However, none of these experimenters has employed rates of shear differing greatly from those of the compression-type plastometers,[8,9,10] which operate at rates much lower than those existing in factory tubing machines. It seemed, then, that this fact might explain why no great discrepancies between extrusion plasticity results and those of the parallel-plate compression-type plastometer were found, at least in so far as could be discovered in the literature. Hence, it was thought desirable, from both an academic and a practical standpoint, to make a study of the flow of rubber through an orifice over a wide range of rates of shear.

Rate of Shear as a Criterion of Flow Conditions

In order that a testing instrument may correlate with factory processes, it is obvious that the flow conditions in the testing instrument should be made to coincide with those in the factory machines. This raises the question as to what physical entity completely describes the flow conditions at a given temperature, either in a factory machine or in a measuring instrument. Two physical quantities are available for use in such a description, the shearing stress F_s and the rate of shear dv/dx where v is the velocity of the plastic material at a distance x from the axis of a capillary through which the material is flowing under a pressure P.

If R be the radius of the capillary and L its length, the shearing stress at the walls is:

$$[F_s]_R = PR/2L \tag{1}$$

The equation relating dv/dx with F_s is sometimes assumed to be

$$dv/dx = ((F_s - f)/c)^n \tag{2}$$

where f is the yield stress; c the consistency; and n a constant for a given material. For $n = 1, f = 0$, (2) becomes the equation of viscous flow in a perfect liquid. For f finite, $n = 1$, (2) becomes the equation of a truly "plastic" material, as defined by Bingham.[11]

The use of the shearing stress F_s as a criterion of flow conditions is forbidden because, in tubing machines, the pressure is in general unknown. Hence we must rely on the rate of shear dv/dx as a criterion of flow conditions. This is apparently a rather logical quantity to use in this connection, for it always has the form of a linear velocity of extrusion divided by the cross-sectional dimension of the orifice. These two major variables determine the rate of extrusion at a given pressure and temperature. Obviously the dependence of dv/dx upon the coördinates makes it necessary to employ some sort of averaging process in order to give a quantity which can be calculated for different orifices and different rates of flow. Consequently a rather arbitrary method of averaging has been employed, namely, that of volume weighting. By definition then the mean rate of shear is:

$$(dv/dx)_{ave} = \int_0^h (dv/dx)A(x,t)dx / \int_0^h A(x,t)dx \tag{3}$$

where v is the linear velocity of extrusion; x the coördinate normal to flow with origin at the center of the orifice. $A(x, t)dx$ is the volume element under the steady state velocity front, in which the rate of shear has a value dv/dx; t is the time, and h the semi-cross-sectional dimension of the orifice. Another assumption must be made in order to compute this integral, *i. e.*, the form of the velocity front. Inasmuch as the velocity front for the case ($n = 1, f \ll F_s$) in Eq. (2) is of substantially parabolic section, it seemed that the assumption of a parabolic section for the general case would not introduce great error into the result. Furthermore, since we are interested chiefly in the relative rates of shear, and the only deviations caused by error in the selection of the type of velocity front are small changes in the constant q in the relation:

$$(dv/dx)_{ave} = qv_{ave}/D \tag{4}$$

where v_{ave} is the mean velocity of extrusion, and D the cross-sectional dimension, there is no necessity for extreme accuracy in our geometrical assumption.

The calculation of the integral (3) is a perfectly straightforward process and yields the results:

$$-(dv/dx)_{ave} = 9v_{ave}/4D \tag{5}[1]$$

for a rectangular slit orifice of infinite length, and

[1] The validity of formulas (5) and (6) has been partially verified by an experiment to be described in a subsequent paper. Efflux rates of tube stock from a slit orifice and a circular orifice mounted in a single extrusion machine were measured simultaneously, *i. e.*, at the same temperature and pressure. Assuming a linear relationship between rate of shear and shearing stress, it was found that the mean rates of shear, as computed for the orifices by (5) and (6), respectively, agreed within 30 per cent, after the proper correction for the fact that the shearing stresses in the two orifices were different, had been applied. Thus, the formulas (5) and (6) give at least the order of magnitude of the relative mean rates of shear for the slit orifice and circular orifice, respectively.

TABLE I

NUMERICAL VALUES OF MEAN RATES OF SHEAR FOR VARIOUS INSTRUMENTS AND MACHINES

Experimenter	Type of instrument	Formulae Used	$\left(\frac{dv}{dx}\right)_{ave}$	Remarks
Griffiths[4]	Extrusion plastometer	(6)	58.5/sec.	Size of die uncertain, piston type
Behre[5]	Extrusion plastometer	(6)	1.28/sec.	Air pressure type
Marzetti[3]	Extrusion plastometer	(6)	1.38/sec.	Air pressure type
Elliot[6]	Extrusion plastometer	(6)	0.54/sec.	Piston type
Martin[7]	Extrusion plastometer	(6)	171/sec.	Piston type, size of die uncertain
—	Williams plastometer	(8)	0.021/sec.	After 1 min. compression
—	Williams plastometer	(8)	0.067/sec.	After 5 min. compression
Van Rossem and Van der Meijden[8]	Goodrich type plastometer	(9)	0.053/sec.	After 1 min. compression
Van Rossem and Van der Meijden[8]	Goodrich type plastometer	(9)	0.022/sec.	After 10 min. compression
Van Rossem and Van der Meijden[8]	Goodrich type plastometer	(9)	0.016/sec.	After 20 min. compression
—	Inner tube machine	(5)	515/sec.	$\bar{v}$ = 20 cm./sec., slit = 0.89 mm.
—	Tread tubing machine	(5)	32.8/sec.	$\bar{v}$ = 18.5 cm./sec., slit = 1.3 cm.
Dillon	Extrusion plastometer	(5)	568/sec.	Piston type

$$-(dv/dx)_{ave} = 64v_{ave}/15D \qquad (6)^1$$

for a circular orifice.

The relation (5) is directly applicable to the compression type of plastometer. For example, in the Williams' plastometer, the flow may be considered as extrusion through a rectangular slit of continuously decreasing width and increasing length. Then, assuming constant volume and Williams' equation

$$yt^n = K \qquad (7)$$

the mean rate of shear at the periphery of the pellet can be shown to be

$$(dv/dy)_{ave} = (9n/8)(V/\pi)^{1/2}(1/K^5)\cdot y^{7/2} \qquad (8)$$

at a given distance of separation of the plates y and where V is the volume of the pellet.

For the Goodrich type of parallel plate plastometer, in which the plates have the same area as the ends of the cylindrical pellet, similar considerations, including Taylor's equation[8]

$$1/y^2 - 1/y_0^2 = kt \qquad (9)$$

where y is the separation of plates at time t, y_0 the original separation of plates at $t = 0$, and k a constant, yield:

$$(dv/dy)_{ave} = 9Rk/16[1/kt + 1/y_0^2)^{1/2}] \qquad (10)$$

where R is the radius of the plates.

Table I gives the numerical values of $(dv/dx)_{ave}$ as computed from the formulas (5), (6), (9), and (10). The values are the maxima for each of the instruments, respectively, except for the authors' plastometer, which can attain a rate of shear somewhat over 1000/sec. with a moderate sacrifice in the accuracy of measurement of the extrusion velocity. The values given for the two types of tubing machines are thought to be typical.

Apparatus

The extrusion plastometer consists essentially of a hardened steel piston which extrudes the rubber through a die at the lower end of a steel cylinder. The piston, which is of 1.27 cm. (1/2 in.) diameter, is operated through a distance of 7.62 cm. (3 in.) by a pneumatic piston of diameter 14 cm. (5 1/2 in.). Thus, air pressures of 0.35 to 0.56 kg./cm.^{2} (5 to 80 lb./in.^{2}) used in the pneumatic cylinder correspond to pressures of 42.5 to 68.0 kg./cm.^{2} (605 to 9680 lb./in.^{2}) exerted on the rubber. The inner diameter of the extrusion cylinder was made 1.59 cm. (5/8 in.) to avoid the jamming which might occur with a snugly fitting piston. The extrusion cylinder was heated electrically. A coil of No. 40 B & S nickel wire was wound underneath the nichrome heating windings, and served as a resistance thermometer. The temperature was controlled manually to within 0.1° C. by manipulating a rheostat in the heating circuit so as to maintain balance in a Wheatstone bridge, one arm of which was the nickel resistance coil. An additional heating coil wound below the die served as a guard ring in preventing downward heat flow across the die. The whole extrusion unit was carefully insulated thermally by means of Bakelite and felt.

The air pressure for operating the pneumatic piston was maintained constant to within 0.017 kg./cm.^{2} (1/4 lb./in.^{2}) by means of a common type of reducing valve. To further stabilize the pressure at high extrusion velocities, a 75.7-liter (20-gal.) steel tank was connected to the air line near the plastometer air inlet.

Small tubing and constrictions were avoided as far as possible, in order to reduce pressure drops. Pressures were measured by a gage of the Bourdon tube type.

The orifice (see Fig. 1) was 3.18 mm. ($^1/_8$ in.) in diameter, and 4.76 mm. ($^3/_{16}$ in.) in length. Its upper end was tapered by means of a 45° cone up to the diameter of the extrusion cylinder. The die plate and the extrusion cylinder were pinned together to prevent relative motion, but to permit quick removal from a yoke which was rigidly attached to a table. The pneumatic cylinder unit and the extrusion piston were screwed into the top of the yoke by means of a pair of helical planes. Smooth ground surfaces on both ends of the extrusion cylinder prevented leakage of rubber.

At the lower rates of flow, the time of extrusion was measured by means of a

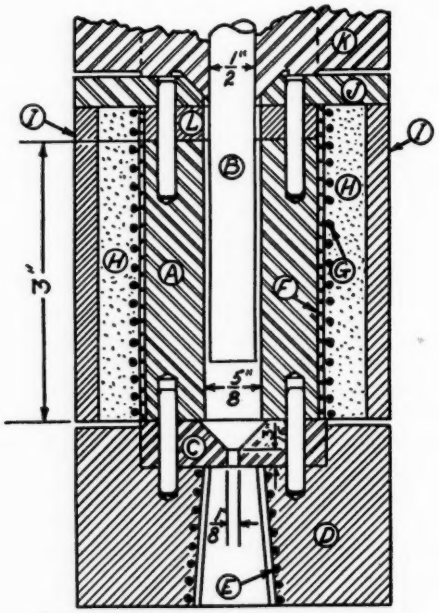

Figure 1—Detail of Extrusion Unit

A, extrusion cylinder; *B*, extrusion piston; *C*, die plate; *D*, Bakelite base; *E*, guard ring heating coil; *F*, nickel resistance coil; *G*, nichrome heating coil; *H*, felt insulation; *I*, Bakelite tube; *J*, steel plate; *K*, rotating upper unit; *L*, Bakelite shim.

stop watch. At the higher rates, a contact device mounted on the tail rod of the pneumatic unit closed an electric circuit at 6 equally spaced points in the stroke, thus actuating an induction coil. The high potential terminal of this coil was connected to a stationary electrode pressed against a sheet of polar coördinate paper fastened on a brass disc which was rotated at 1 r. p. m. by a synchronous motor. Thus at 6 equally spaced points of the stroke, a small hole was burned in the coördinate paper. From this series of points, the total time of extrusion, and the degree of uniformity of the extrusion velocity were known.

Extruded samples were weighed to within 0.01 gram and, from the specific gravity of the stock, the extruded volume was computed. The rate of efflux was then calculated as the quotient of the volume extruded and the time of extrusion.

For loading the cylinder, rubber pellets were cut out by means of a rotating cylindrical cutter. This cut the samples in the form of a cylinder of 1.51 cm. ($^{19}/_{32}$ in.) diameter and length limited only by the thickness of the sheet of rubber from which they were cut. These samples slipped readily into the 1.59 cm. ($^{5}/_{8}$ in.) bore of the extrusion cylinder.

For all the stocks thus far tested, the rubber was found to come up to temperature in 20 minutes or less. Hence, this heating time was adopted as a standard. When only a few extrusions were to be made, the rubber was placed in the cylinder and allowed to stand at the desired temperature for 20 minutes without additional preheating. When it was desired to run a large number of samples, they were conditioned in oil-tight sheet metal air chambers mounted in a thermostatically controlled oil bath, set at the correct temperature, for 20–40 minutes and then transferred quickly to the extrusion cylinder where they were kept for 8–10 minutes to compensate for any temperature drop during transfer.

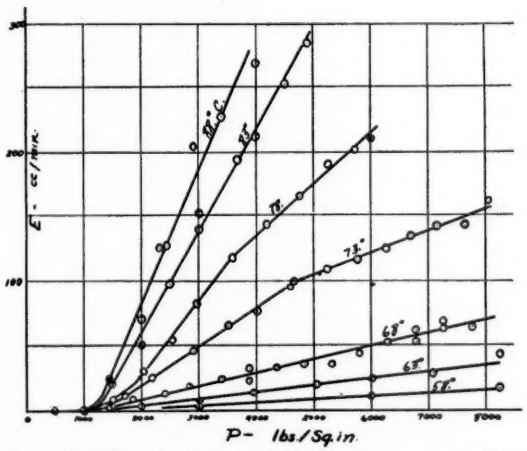

Figure 2—Efflux Rate as a Function of Pressure. Tread Stock No. 1

Procedure

After the preheated rubber samples were transferred to the extrusion cylinder and tamped in so as to fill it completely, the pneumatic unit was put in place. After six minutes of standing in the cylinder, the piston was slowly lowered so as to extrude a short segment of rubber and squeeze out most of the air occluded in the rubber. After one or two minutes, the time allowed to compensate for any small departure from thermal equilibrium caused by the motion of the piston, air was admitted to the upper end of the pneumatic cylinder and the extrusion was made, the time of extrusion being recorded. Immediately after the extrusion, the air was admitted to the lower end of the pneumatic cylinder, to raise the piston. The pneumatic unit was then removed, the annulus of rubber remaining in the cylinder was pulled out by means of a hook, and the extruded segment was removed. The length of the extruded segment was measured before cooling. The measurement of length gives an inverse measure of the amount of recovery.

Results

It is now quite generally conceded that there are at least two quantities necessary to define the plastic state of a material, *i. e.*, the mobility μ ($\equiv 1/c$ in Equation (2)) and the yield stress f. In general, for a given material, both μ and f are functions of temperature. The method used for studying the dependence of these quantities[2] on the other variables (*i. e.*, type and degree of rubber pigmentation, degree of breakdown of the rubber, etc.) was that of measuring the rate of efflux as a function of driving pressure at constant temperature.

Highly compounded stocks, such as tread stocks, were found to give simpler flow relations than lightly compounded stocks (tube stocks) or crude rubber.

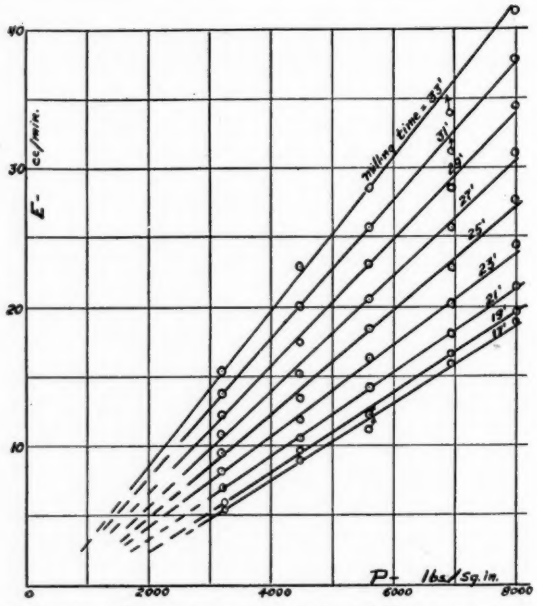

Figure 3—Efflux Rate as a Function of Pressure. Tread Stock No. 2. Temperature 78° C.

Hence, the various types of stocks are discussed in the order of the simplicity of the laws of flow which they obey, rather than in the order of the degree of compounding.

The curves giving the rate of efflux E as a function of pressure P for the moderately hard tread stock No. 1 (carbon black 24.4 per cent by volume on rubber, accelerator-mercaptobenzothiazole) are shown in Fig. 2.

It is seen that the isothermals attain linearity at rather low pressures. The slopes of the various isothermals are radically different, showing that the mobility μ is a rapidly increasing function of temperature. A slight change in slope of the linear portions of the 73° and 78° C. isothermals is quite definite, and is reproducible, but is yet to be explained. The curves of Fig. 2 are typical of those for

[2] It should be noted that, because of slippage and the residual elasticity of the rubber, the absolute values of μ and f cannot be calculated from the efflux rate-pressure curves and no attempt was made to obtain numerical values for either quantity.

all tread stocks tested, except that the anomalous change in slope does not always appear.

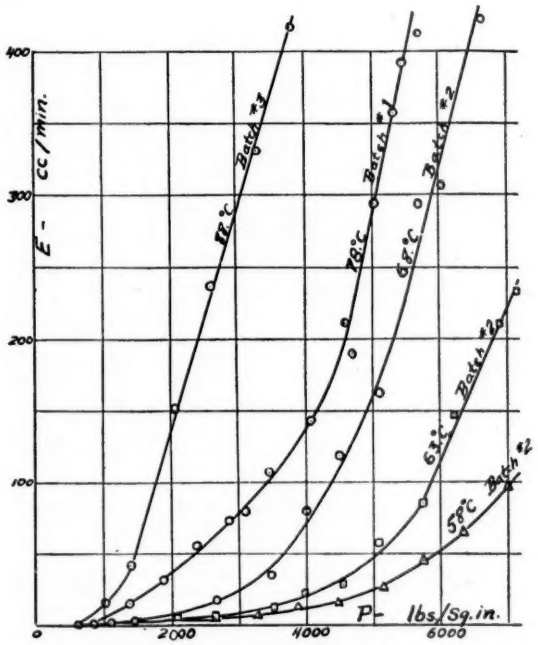

Figure 4—Efflux Rate as a Function of Pressure. Tube Stock No. 1 (Gray)

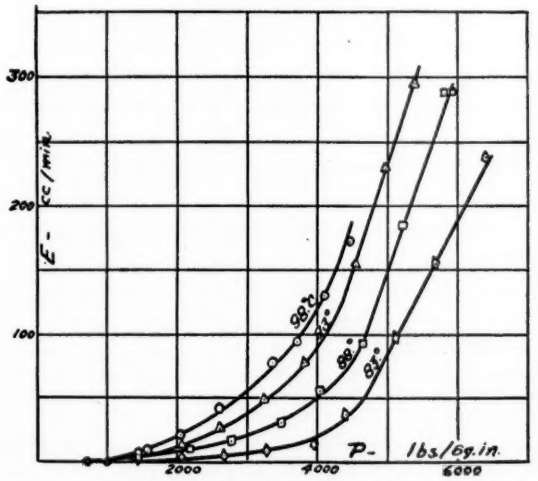

Figure 5—Efflux Rate as a Function of Pressure. Crude Rubber (Mill Massed)

The curves of Fig. 3 were obtained from samples taken off the mill after different periods of the mixing of a single batch of tread stock No. 2 (carbon black

26.1 per cent by volume on rubber, accelerator-mercaptobenzothiazole). All the observations were made at 78° C. in this case. Linearity at higher pressures again appears.

Figure 4 is a set of E-P isothermals for a gray tube stock No. 1 (blanc fixe—3.2 per cent by volume on rubber, accelerator-aldehyde-amine). The curves are

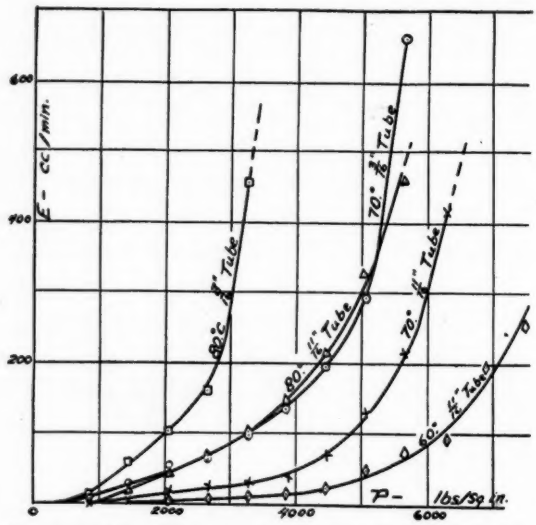

Figure 6—Efflux Rate as a Function of Pressure. Tube Stock No. 1

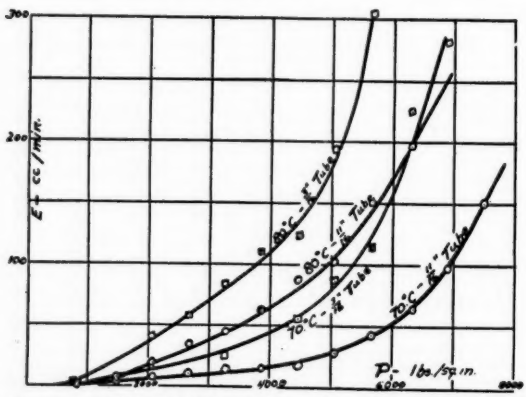

Figure 7—Efflux Rate as a Function of Pressure. Tube Stock No. 2 (Red)

distinctly different from those obtained with tread stocks, for linearity is reached only at much higher pressures. Furthermore, after reaching linearity, the curves become nearly parallel. The curves for crude rubber which had been milled, cooled, and then remilled (Fig. 5) show this effect in a still more pronounced form.

This parallelism of the linear portions of the E-P curves for tube stocks and crude rubber at first suggested that the die, which was only 4.76 mm. ($^3/_{16}$ in.) in length,

behaved as an orifice in regard to these softer stocks rather than as a tube. To investigate this possibility, a new die was made, of the same diameter 3.18 mm. ($^1/_8$ in.) but 17.4 mm. ($^{11}/_{16}$ in.) in length. As can be seen from Figs. 6 and 7[3]

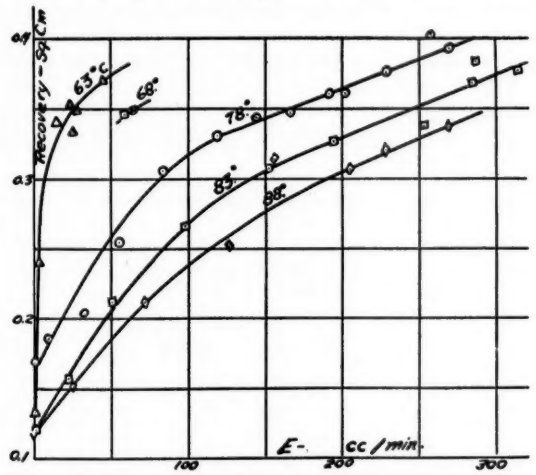

Figure 8—Recovery as a Function of Efflux Rate. Tread Stock No. 1

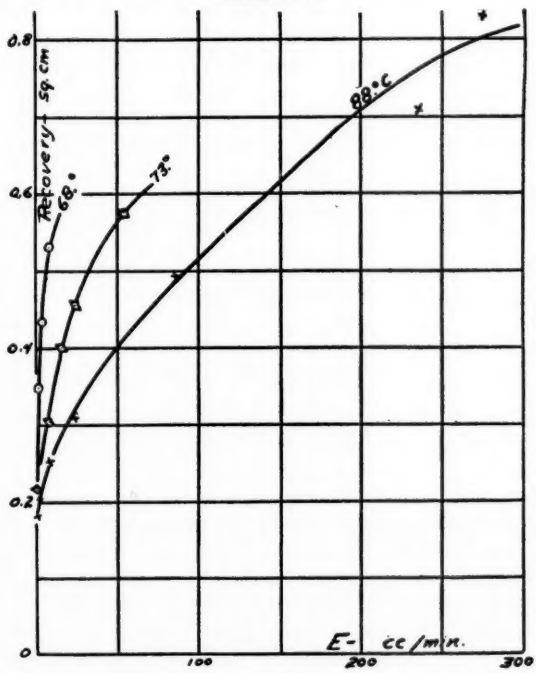

Figure 9—Recovery as a Function of Efflux Rate. Tube Stock No. 1

[3] The curves of Fig. 7 apply to a red tube stock No. 2 (blanc fixe—7.1 per cent by volume on rubber, accelerator diphenylguanidine).

no great change in the form of the E-P curves was observed with the longer tube. The parallelism of the linear portions of the curves is preserved with the longer tube, though the slope is slightly different for the two dies. It seems fair, then, to consider this type of curve to be characteristic of the softer stocks and to depend only slightly upon the type of die used. The ordinates are diminished considerably with the longer tube but not in the ratio of the lengths of the respective tubes. Thus it appears that a large fraction of the shear occurs in the rubber as it flows in the conical entrance to the die tube.

The peculiar form of the E-P curves for soft stocks may be interpreted to mean

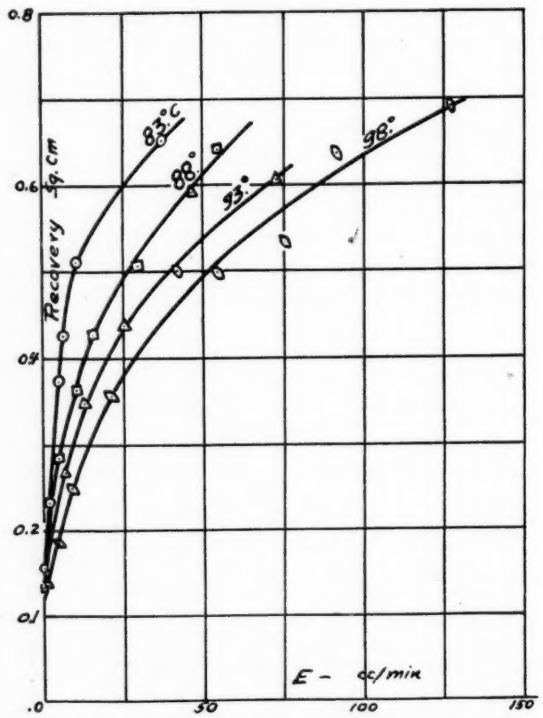

Figure 10—Recovery as a Function of Efflux Rate. Crude Rubber (Mill Massed)

that the mobility is independent of temperature, at least in the region of rates of shear described by the linear portions of the curves. This then may partially explain why the compression type plastometer, which measures the mobility at low rates of shear, often fails to correlate with factory extrusion machines employing a high rate of shear.

The relation between "recovery" and rate of efflux is given in Figs. 8, 9, and 10. "Recovery" is defined as proportional to the average cross-sectional area of the extruded segment. The length of each segment was measured immediately after extrusion and, from knowledge of the mass extruded and the specific gravity, the average cross-sectional area was computed. The curves are

all of the same type, recovery increasing with rate of efflux and decreasing with temperature.

A somewhat more practical study was made with the plastometer in investigating the rate of efflux as a function of milling time. For this purpose, rubber batches were mixed on the factory 214 cm. (84 in.) mills according to standard factory specifications except that the milling was carried much beyond the standard time. Counting zero milling time as that time at which the first of the master batches was thrown on the rolls in the case of the compounded stocks, and as the time at which the unmilled crepe was thrown on, in the case of the crude rubber,

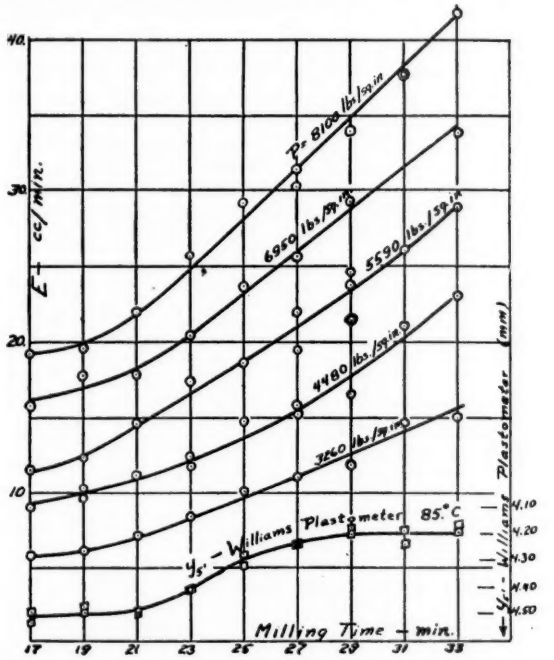

Figure 11—Efflux Rate as a Function of Milling Time. Tread Stock No. 2. Temperature 78° C.

samples were cut off at the intervals indicated in Figs. 11, 12, and 13. The stock was allowed to cool in flat sheets in air for one hour. Observations were then made both with the extrusion plastometer and the Williams' instrument.

The efflux-rate *vs.* milling-time curves for the extrusion plastometer are all of similar nature, showing a rapid and nearly linear increase of efflux rate with milling time. For tread stocks, the curve for the Williams' plastometer flattens out at higher milling times. This same tendency is exhibited for crude rubber but not to so great a degree. The curves demonstrate that the extrusion plastometer, when operated at sufficiently high pressures, is more sensitive than the Williams' plastometer in detecting "overmilling." Furthermore, the extrusion instrument is more sensitive to overmilling in tread stocks than in tube stocks.

Sources of Error

1. *Regularity of the Flow.*—In computing the mean rates of shear in this work, a velocity front of parabolic section was assumed. Because of the deformation

which the rubber undergoes in the extrusion cylinder before entering the die, it did not seem possible to determine experimentally the shape of the velocity front. However, a simple experiment was performed which shows that the flow is regular and is symmetrical about the axis of the die tube. The experiment consisted in placing thin calendered white stock between the pellets of tread stock or red tube

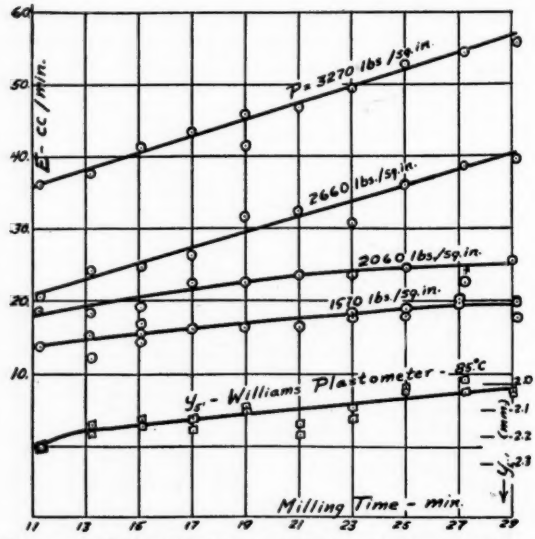

Figure 12—Efflux Rate as a Function of Milling Time. Tube Stock No. 1. Temperature 68° C.

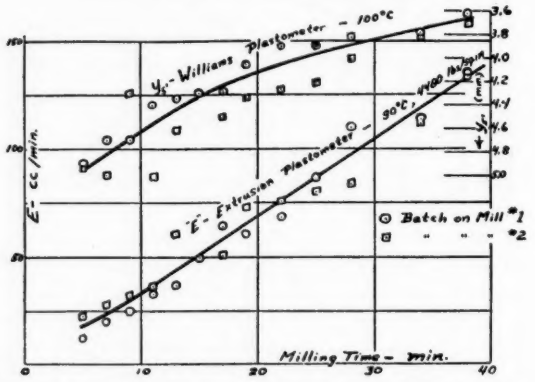

Figure 13—Efflux Rate as a Function of Milling Time. Crude Rubber

stock before they were inserted in the extrusion cylinder. The stock was extruded and cured, after which it was cut along its axis. Figure 14 is a photostat of four of these laminated extrusions, two of which (*c* and *d*) are of tread stock and two of red tube stock (*a* and *b*). To draw conclusions from these flow figures other than that the flow is regular and symmetrical about the axis of the tube seems unjustified.

2. *Correction for Friction in the Pneumatic Unit.*—The ratio of the area of the pneumatic piston to that of the 1.27 cm. ($^1/_2$ in.) piston is $(14.0/1.27)^2 = 121$. Hence, if there were no friction in the pneumatic unit, for a given efflux rate E, the pressure on the rubber would be:

$$P_E = 121 \cdot P_{E'} \tag{11}$$

where $P_{E'}$ is the pressure gage reading. For the actual case where there is a frictional force equivalent to a back pressure $P_{E''}$

$$P_E = 121 \cdot (P_{E'} - P_{E''}) \tag{12}$$

The quantity of $P_{E''}$ was determined by running the plastometer with no rubber

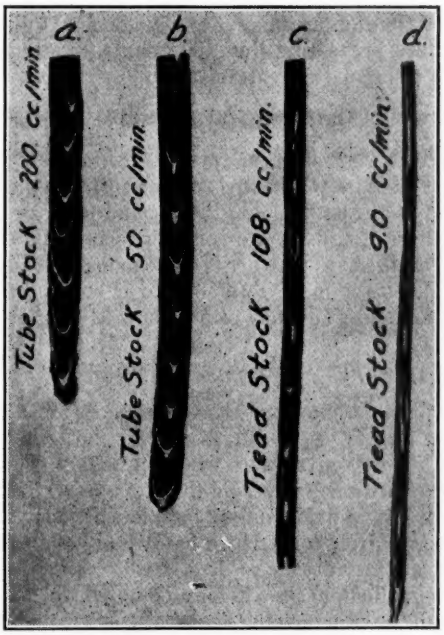

Figure 14—Photostat of Laminated Extrusions to Show Regularity of the Flow

in the extrusion cylinder, at low air pressure, measured both by the gage and by a mercury manometer, and measuring the velocity of the piston with the timing device. A curve was plotted giving the observed values of $P_{E''}$ as a function of E. Thus, for any efflux rate E, the proper value of $P_{E''}$ could be read from the curve and subtracted from the observed gage reading to give the pressure on the rubber by Eq. (12).

3. *Effect of Shear in Rubber Annulus between Piston and Inner Wall of Extrusion Cylinder.*—The diameter of the extrusion piston was made 3.18 mm. ($^1/_8$ in.) less than that of the extrusion cylinder, so as to avoid "jamming" at high pressures. This could occur with a tightly fitting piston, particularly when using heavily compounded stocks. Consequently, there was reason for some concern as to

whether or not a large fraction of the total shearing force was used in shearing the rubber annulus between the piston and the inner wall of the cylinder.

Suppose the whole of the shearing force were utilized in shearing the rubber in the annulus. Then the velocity of the piston would continuously decrease during the extrusion because of the linear increase of shearing area between piston and cylinder. For the actual case, where part of the force shears the rubber in the annulus and part extrudes the rubber through the die, the distribution of the total force between the annulus and the extruding rubber can be computed by measuring the velocity at several points in the stroke. Using the results of a large number of extrusions (as recorded by the timing device), it was thus found that not more than 15 per cent of the total force was utilized in shearing the rubber annulus.

4. *Effect of Premature Vulcanization in the Extrusion Cylinder.*—For all the stocks employed in this work, careful observations were made of the extrusion rate as a function of time of heating. No decrease in the extrusion rate was observed in the standard preheating time (20 minutes) and hence it may be concluded that the effect of premature vulcanization, for these stocks, was negligible.

Mathematical Appendix

For an accurate derivation of the mean rate of shear in a material flowing through a tube or orifice, it is necessary to know (*a*) the form of the velocity front and (*b*) the degree of slip at the walls. The flow conditions for rubber in the plastometer, which has been described, are somewhat complex since rubber stocks possess considerable elasticity. Furthermore the degree of slip has not as yet been investigated. When the mean rate of shear is computed from the equation of plastic flow which embodies the idea of plug flow as suggested by Buckingham, *i. e.*,

$$v = \mu[(P/4L)(R^2 - r^2) - f(R - r)]$$

where v is velocity of plastic material at a distance r from the axis of the tube, R is the radius of the tube, L is the length of the tube, μ is the mobility, and P the applied pressure, dv/dr is given as a function of f, μ, P, L, R and the maximum velocity of flow v_m. Since f is very difficult to determine in rubber, because of the presence of elasticity and slip and, in fact, has little meaning for tube stocks and crude rubber, the resulting formula for dv/dr is of little practical use. Hence to obtain an approximate formula for dv/dr, it was necessary to assume a parabolic velocity front, and no wall slippage. It may be noted that, since the efflux rate-pressure curves become approximately linear at high rates of flow and at high temperatures (see Figs. 2, 3, 4, 5), the velocity front should be nearly parabolic under those conditions which are of most practical importance in tubing machines.

Mean Rate of Shear—Rectangular Slit.—For a rectangular slit of length l, then, assuming a parabolic velocity front and no wall slippage, and neglecting the shear at the ends of the slit, if v be the velocity of flow at a distance x from the center of the slit, v_m be the maximum velocity, h the semi-cross-sectional dimension, and k a constant;

$$v = k(h^2 - x^2), \quad v_m = kh^2$$

Here, the factor $A(x, t)dx$ of Eq. (3) is $vtldx$ and the volume-weighted mean rate of shear is:

$$s_{ave} = -\left(\frac{dv}{dx}\right)_{ave} = \frac{t \cdot l \int_0^h -(dv/dx)vdx}{t \cdot l \int_0^h vdx} = \frac{\int_0^h 2x \cdot k \cdot (h^2 - x^2)dx}{\int_0^h k \cdot (h^2 - x^2)dx} = \frac{3}{4}\frac{v_m}{h} \qquad (4)$$

Now, to put s_{ave} in terms of the mean velocity v_{ave}, we write

$$v_{ave} = \frac{\int_0^h v dx}{\int_0^h dx} = \frac{\int_0^h k(h^2 - x^2)dx}{h} = \frac{2}{3} v_m \tag{5}$$

Thus:

$$s_{ave} = -(dv/dx)_{ave} = (9/4)v_{ave}/D \tag{6}$$

where $D = 2h$.

Mean Rate of Shear—Circular Orifice.—Assuming that the velocity front is a paraboloid of revolution and that there is no wall slippage, if h be the radius of the tube;

$$v = k(h^2 - r^2); \quad v_m = kh^2$$

Here, for volume weighting, the factor $A(x, t)dx$ is $2\pi \cdot r \cdot v \cdot t \cdot dr$. Thus:

$$s_{ave} = -\left(\frac{dv}{dr}\right)_{ave} = \frac{2\pi t \int_0^h -(dv/dr) v \cdot r dr}{2\pi t \int_0^h v \cdot r \cdot dr} = \frac{\int_0^h 2r^2(h^2 - r^2)d_r}{\int_0^h r(h^2 - r^2)dr} = \frac{32}{15}\frac{v_m}{D} \tag{7}$$

where $D = 2h$. The mean velocity, weighted by the element of cross-sectional area, is

$$v_{ave} = \int_0^h v \cdot r dr / \int_0^h r \cdot dr = \int_0^h k(h^2 - r^2) r dr / {}^1/_2 h^2 = {}^1/_2 v_m \tag{8}$$

Thus:

$$s_{ave} \equiv -(dv/dr)_{ave} = (64/15)v_{ave}/D \tag{9}$$

Mean Rate of Shear—Williams' Parallel Plate Plastometer.—Consider the flow of plastic material between parallel plates when the separation at time t is y, the radius of the pellet being r. The flow may be considered as extrusion through a rectangular slit of continuously decreasing width and increasing length. If we assume a parabolic velocity front, no slip at the plates, and Williams' equation[10]

$$yt^n = K \tag{16}$$

where K and n are constants, we obtain upon differentiating with respect to t,

$$v_y = dy/dt = -ny/t = -nK/t^{n+1} \tag{18}$$

which is the velocity of the moving plate. Now, to calculate the radial velocity v_r, we consider the pellet as a circular disc. Then the volume of the disc is

$$V = \pi r^2 y = \text{const.}$$

Then

$$dV = 2\pi r y dr + \pi r^2 dy = 0$$

or

$$v_r = \frac{dr}{dt} = -\frac{r}{2y}\frac{dy}{dt} = \frac{n}{2}\frac{r}{t} = \frac{n}{2}\left(\frac{V}{\pi}\right)^{1/2}\frac{1}{y^{1/2} \cdot t}$$

Hence, the mean velocity of the rubber at the periphery is

$$v_{ave} = v_r = \frac{n}{2}\left(\frac{V}{\pi}\right)^{1/2}\frac{1}{y^{1/2} \cdot t} \tag{19}$$

From Eq. (6) for a static slit orifice the rate of shear is given as a function of y and t. Thus

$$s_{ave}(y, t) = -\left(\frac{dv}{dy}\right)_{ave}\frac{9}{4}\frac{v_{ave}}{y} = \frac{9}{4}\frac{n}{2}\left(\frac{V}{\pi}\right)^{1/2}\frac{t^{3n/2-1}}{K^{3/2}} \tag{21}$$

Williams[10] gives $n \cong 0.2$, so that the mean rate of shear over the periphery of the pellet is

$$s_{ave}(t) \cong \frac{9}{8}\frac{k}{K^{3/2}}\left(\frac{V}{\pi}\right)^{1/2} t^{-0.7} = \frac{9}{8}\left(\frac{V}{\pi}\right)^{1/2}\frac{n}{K^5}\frac{y^4}{y^{1/2}} \qquad (8)$$

Mean Rate of Shear—Goodrich Type Parallel Plate Plastometer.—Consider the flow of a pellet of radius R of plastic material between plates of radius R with a separation y at time t. If we assume a parabolic velocity front, no slip at the plates, shear negligible in the bulged portion, *i. e.*, R = const. and Taylor's equation:[7]

$$1/y^2 - 1/y_0^2 = kt \qquad (23)$$

where y is the final thickness of pellet at time t, y_0 the initial thickness of pellet at time o, $k \equiv 4mg/3\eta\pi(2R)^4 \equiv$ const., mg the downward force on top plate, η the viscosity of rubber; we have, upon differentiating with respect to t,

$$dy/dt = -ky^3/2 \qquad (25)$$

so, if the volume of the disc is $V = \pi R^2 y$,

$$dV = \pi R^2 dy \qquad (26)$$

The rate of efflux is

$$dV/dt = \pi R^2 dy/dt = -(v_r)_{ave} 2\pi R y \qquad (27)$$

where $(v_r)_{ave}$ is the mean radial velocity of the rubber. Hence, from (27) and (25),

$$(v_r)_{ave} = Rky^2/4 \qquad (28)$$

The flow, for this instrument, is roughly equivalent to extrusion through a rectangular slit of varying width but constant length. Thus, we can use again expression (6) to obtain the mean rate of shear

$$s_{ave}(y) = -(dv/dx)_{ave} = 9(v_r)_{ave}/4y = 9Rky/16 \qquad (29)$$

or, from (23),

$$s_{ave}(t) = (9Rk/16)1/(kt + 1/y_0^2)^{1/2} \qquad (10)$$

The value of k is found by plotting t against $1/y^2$, using experimental data. The slope of the of the linear curve obtained is than $1/k$.

References

[1] B. Marzetti, *India Rubber World*, **68**, 776 (1923).
[2] B. Marzetti, *Rubber Age* (London), **6**, 139 (1925–26).
[3] B. Marzetti, *Rubber Age* (N. Y.), **15**, 454 (1924).
[4] R. W. Griffiths, *Trans. Inst. Rubber Ind.*, **1**, 308 (1925–26).
[5] J. Behre, *Kautschuk*, **8**, 2 (1932); RUBBER CHEM. & TECH., **6**, 244 (1933).
[6] F. Elliott, *Trans. Inst. Rubber Ind.*, **3**, 468 (1927–28).
[7] G. Martin, *Ibid.*, **6**, 298 (1930).
[8] Van Rossem and Van der Meijden, RUBBER CHEM. & TECH., **1**, 393 (1928).
[9] E. Karrer, *Ind. Eng. Chem.*, **21**, 770 (1929); RUBBER CHEM. & TECH., **2**, 592 (1929).
[10] Williams, *Ibid.*, **16**, 362 (1924).
[11] E. C. Bingham, "Fluidity and Plasticity," **1922**.

[Reprinted from Transactions of the Institution of the Rubber Industry, Vol. 9, No. 3, pages 196–204, October, 1933.]

The Effect of Temperature on the Plasticity of Rubber

R. D. Prestwich

Department of Chemistry and Rubber Technology, Northern Polytechnic, London

The aim of the investigation was to investigate the effect of temperature on the plasticity of rubber before and after compounding.

Review of Previous Work

Marzetti (*Rubber Age*, **6,** 139 (1925)), using an extrusion plastometer, found that above a temperature of 50° C., an approximately linear relationship existed between the temperature and the square root of the weight of rubber extruded in a definite time.

De Visser ("Unvulcanized Rubber," **1926,** page 84) gave figures for the plasticity of calendered sheet rubber at temperatures below 70° C. According to him, the change in shape of a compressed piece of unvulcanized rubber is permanent if the compression is carried out above 70° C. The apparatus used was a modified Williams parallel plate plastometer.

van Rossem (*Rubber Age* (N. Y.), **23,** 438 (1928)), using a similar apparatus, carried out a series of tests on masticated rubber at temperatures ranging from 16° to 70° C. The elastic recovery of the rubber was considerable at temperatures below 70° C.

Procedure

A parallel plate plastometer (designed by the Research Association of British Rubber Manufacturers) was used in the investigation, with a total load of five kilograms on the pieces under test. The apparatus was contained in a thermostatically controlled water oven.

Spherical samples of such a weight that their volumes were in each case 2 cc. were cut from the mixes employed, and preheated for 15 minutes in the oven before compression, which was carried out between thin cigarette papers. The original thickness of the samples was 15.62 mm. Readings of the thickness were taken after six and twelve minutes' compression.

The temperature range, with the first series of tests, was approximately 43° to 80° C. Considerable variation in readings was observed at the lower temperature owing to difficulty in controlling the temperature, and later series were commenced at temperatures of the order 55–65° C., with a maximum of 80–90° C.

The mixes, after thorough mastication, were left for a period of eleven days before being tested.

The figures representing the plasticity were obtained by employing the Williams' plasticity formula, $K = yx^n$, where y is the thickness in millimeters of a sample after x minutes' compression. K is the reciprocal of the plasticity, *i. e.*, K increases as the stock becomes less plastic. The value of n was calculated for each sample of rubber and each temperature by solving the equation for two values of x and y.

The values of K thus obtained from Williams' formula were compared with the corresponding temperatures.

Variation of Plasticity of Masticated Pale Crepe with Temperature

The first series of observations was carried out on well masticated pale crepe rubber, and the results are given in Table I, and are shown diagrammatically in Fig. 1.

TABLE I

Temp., ° C.	Thickness, 6 Min.	Thickness, 12 Min.	n	K	Log K	Log t	Log K + b Log t	Average of a
49	2.31	2.03	0.186	3.229	0.5092	1.6902	1.8257	
54.5	2.10	1.84	0.192	2.958	0.4710	1.7364	1.8254	
61	1.94	1.70	0.190	2.719	0.4345	1.7856	1.8270	1.8263
66	1.75	1.51	0.212	2.558	0.4078	1.8195	1.8270	
75	1.57	1.36	0.210	2.292	0.3602	1.8751	1.8228	
79.5	1.53	1.34	0.200	2.219	0.3459	1.9004	1.8282	

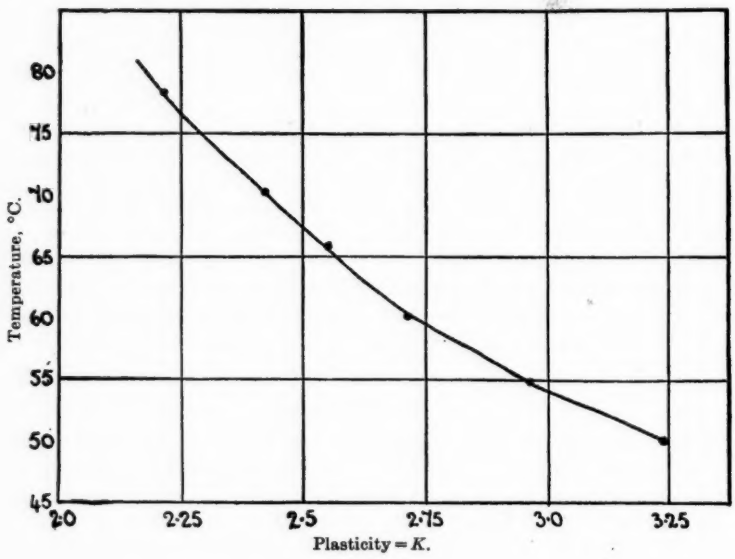

Figure 1

From the hyperbolic curve indicated in Fig. 1, it was concluded that the logarithms might indicate a more easily interpreted relationship than the curve of Fig.1.

If the respective logarithms of the temperature and of K are plotted, Fig. 2 is obtained, from which it is seen there is a straight line relationship between the corresponding logarithms. Hence the equation representing the relationship is of the form

$$\log K = a - b \log t$$

or

$$K = \frac{a}{t^b}$$

In Table I, the values of log K and log t, and also of a and b are given, from which it will be observed that a is almost constant at 1.826, and b is similarly almost constant at 0.78.

It is interesting to note that if the Fahrenheit scale of temperature is used, the value of b is unity (see Table II).

TABLE II

Temp., ° F.	Log t	Log K	Log t + Log K
120.2	2.0799	0.5192	2.5891
130.1	2.1142	0.4710	2.5852
141.8	2.1516	0.4345	2.5861
150.8	2.1783	0.4078	2.5861
167.0	2.2227	0.3602	2.5829
175.1	2.2431	0.3459	2.5890

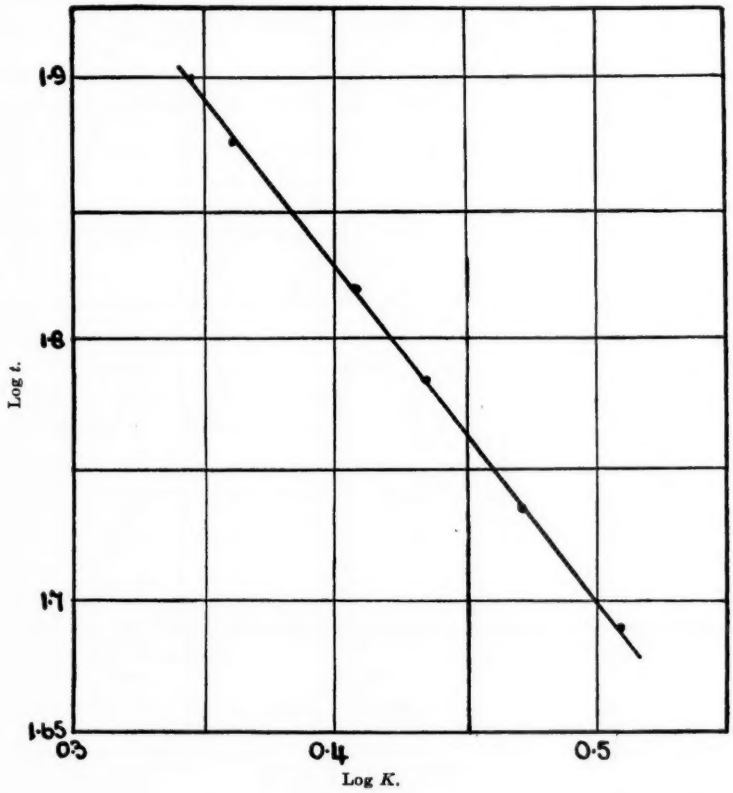

Figure 2

The Effect of the Period of Resting of the Masticated Stock Before Testing

To determine the effect of the period of resting of the masticated stock on the observed plasticity characteristics, a sample of a compounded stock containing 10 volumes of china clay (Stockalite) was cut into two pieces.

One piece was tested 4 days after mixing and the other 11 days after mixing. The results are given in Table III and graphically in Fig. 3.

In Fig. 3 the respective logarithms of the values of K and temperature have been plotted, and it will be observed that the time of resting has an appreciable effect

on the plasticity at any one temperature. On the other hand the graphs are parallel straight lines, and therefore the value of b in the equation $K = \frac{a}{t^b}$ is constant and approximates close to 0.78, and the value of a differs for each corresponding temperature by an amount approximately equal to 0.03.

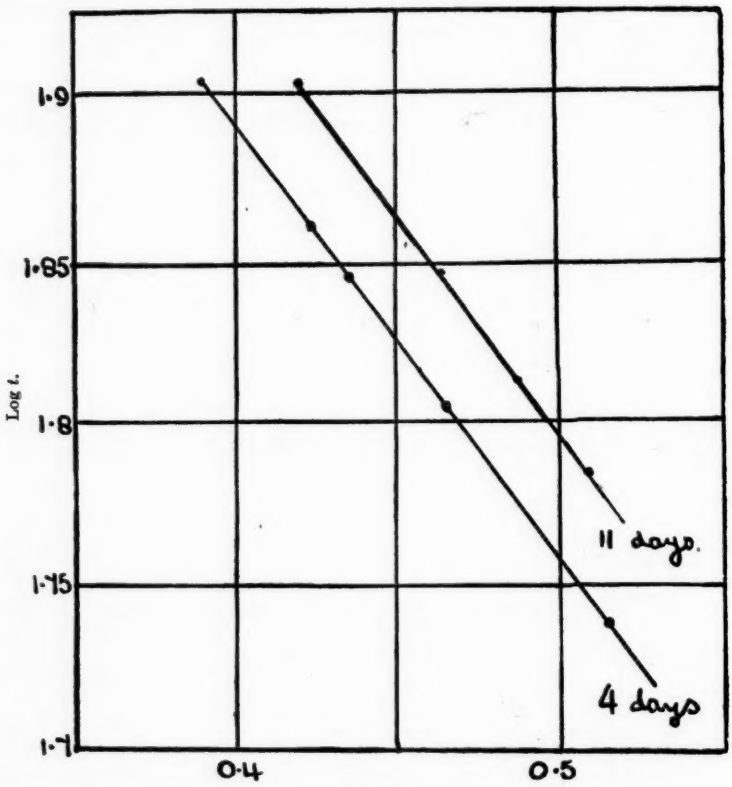

Figure 3

TABLE III

Temp., °C.	Thickness, 6 Min.	Thickness, 12 Min.	n	K	Log K	Log t	Log K + b log t	Average of a
				After 4 Days' Resting				
55	2.24	1.93	0.214	3.285	0.5166	1.7404	1.8741	
64	2.01	1.74	0.208	2.917	0.4649	1.8062	1.8737	
70	1.85	1.59	0.218	2.752	0.4396	1.8451	1.8788	1.8788
76	1.73	1.48	0.225	2.589	0.4131	1.8808	1.8801	
80	1.65	1.41	0.226	2.471	0.3929	1.9031	1.8773	
				After 11 Days' Resting				
61	2.29	2.00	0.195	3.246	0.5114	1.7853	1.9039	
65	2.13	1.85	0.203	3.063	0.4862	1.8129	1.9002	
70	2.01	1.74	0.208	2.917	0.4649	1.8451	1.9041	1.9047
76	1.88	1.62	0.214	2.757	0.4404	1.8808	1.9074	
80	1.80	1.55	0.216	2.651	0.4234	1.9031	1.9078	

TABLE IV

Temp., ° C.	Thickness, 6 Min.	12 Min.	n	K	Log K	Log t	Log K + b log t	Average of a
43.3	2.99	2.64	0.172	4.038	0.6062	1.6365	1.8828	
49	2.66	2.33	0.182	3.678	0.5657	1.6902	1.8840	
59.5	2.25	1.96	0.192	3.159	0.4995	1.7745	1.8836	
65	2.00	1.72	0.217	2.948	0.4696	1.8129	1.8836	1.8841
75	1.81	1.55	0.215	2.644	0.4223	1.8751	1.8849	
80	1.73	1.49	0.212	2.523	0.4002	1.9031	1.8846	
TABLE V								
61.5	2.09	1.80	0.215	3.071	0.4873	1.7889	1.8826	
71.5	1.91	1.66	0.202	2.743	0.4381	1.8543	1.8844	1.8826
82.0	1.71	1.49	0.199	2.443	0.3879	1.9138	1.8807	
TABLE VI								
62	2.11	1.84	0.192	3.002	0.4774	1.7924	1.8755	
71.5	1.70	1.67	0.186	2.651	0.4234	1.8543	1.8697	1.8731
82	1.75	1.55	0.177	2.406	0.3813	1.9138	1.8741	
TABLE VII								
62	1.98	1.74	0.186	2.762	0.4412	1.7924	1.8394	
71	1.80	1.58	0.187	2.515	0.4005	1.8513	1.8445	1.8408
80.5	1.59	1.39	0.194	2.251	0.3523	1.9058	1.8388	
TABLE VIII								
62	1.96	1.72	0.188	2.744	0.4383	1.7924	1.8364	
71	1.72	1.50	0.197	2.447	0.3887	1.8513	1.8327	1.8355
79.5	1.67	1.47	0.184	2.265	0.5550	1.9004	1.8373	
TABLE IX								
64	1.45	1.26	0.202	2.082	0.3184	1.8062	1.7272	
73.5	1.33	1.16	0.197	1.892	0.2771	1.8663	1.7228	1.7248
86	1.14	0.99	0.204	1.644	0.2157	1.9345	1.7246	
TABLE X								
64	2.04	1.87	0.116	2.492	0.3966	1.8062	1.8055	
74	1.81	1.67	0.116	2.228	0.3479	1.8692	1.8068	1.8050
85	1.63	1.51	0.110	1.985	0.2977	1.9294	1.8026	
TABLE XI								
65	2.91	2.76	0.076	3.334	0.5229	1.8129	1.3568	
74	2.78	2.65	0.069	3.145	0.4976	1.8692	1.3574	1.3566 (b 0.46)
84	2.65	2.54	0.061	2.992	0.4706	1.9243	1.3558	
TABLE XII								
65	4.42	4.28	0.046	4.797	0.6810	1.8129	1.0979	
74	4.30	4.17	0.044	4.651	0.6676	1.8692	1.0975	1.0976
85	4.18	4.06	0.042	4.506	0.6538	1.9294	1.0975	(b 0.23)
TABLE XIII								
65	1.75	1.55	0.175	2.394	0.3791	1.8129	1.7931	1.7936
88	1.38	1.22	0.177	1.894	0.2774	1.9445	1.7941	
TABLE XIV								
65.5	1.78	1.57	0.181	2.461	0.3912	1.8162	1.8088	
74	1.63	1.44	0.179	2.247	0.3515	1.8692	1.8094	1.8096
87.3	1.43	1.26	0.182	1.981	0.2968	1.9410	1.8108	
TABLE XV								
65.66	1.55	1.36	0.188	2.169	0.3363	1.8173	1.7538	
74.5	1.39	1.21	0.200	1.989	0.2986	1.8722	1.7589	1.7550
88	1.26	1.11	0.180	1.720	0.2356	1.9445	1.7523	

The effect of increasing the time of resting from 4 to 11 days was to increase the value of log K by a constant amount, that is, the plasticity diminished and K increased.

Hence in all subsequent experimental work, the period of resting after mastication was standardized at 11 days.

Variation of Plasticity with Temperature of Compounded Rubber Stocks

The following mixes stated in volumes were employed to determine the relationship between the plasticity and the temperature of compounded rubber stocks.

Mix No.	4	5	6	7	8	9	10	11	12
Rubber	100	100	100	100	100	100	100	100	100
Whiting	10	...	...	...	...	...	...	...	...
China clay	...	0	10	15	20	...	...	...	...
Carbon black	...	...	...	...	...	0	10	20	30
Zinc oxide	...	...	...	...	...	...	...	...	...

Mix No.	13	14	15	16	17	18	19	20
Rubber	100	100	100	100	100	100	100	100
Whiting	...	...	...	...	...	...	...	...
China clay	...	...	...	...	...	...	...	...
Carbon black	...	...	...	...	...	...	...	...
Zinc oxide	0	$2^1/_2$	5	10	0	10	20	30

The method adopted was to mix all samples on experimental rolls (except in the case of the carbon black stocks, which were made up from a master batch mixed in an internal mixer) at approximately 75° C. for 40 minutes, and test after a rest period of 11 days. The readings obtained are given in Tables IV to XX.

TABLE XVI

Temp., ° C.	Thickness, 6 Min.	Thickness, 12 Min.	n	K	Log K	Log t	Log K + b log t	Average of a
65.66	1.58	1.38	0.195	2.241	0.3503	1.8173	1.7678	
73.5	1.46	1.28	0.198	2.052	0.3122	1.8663	1.7679	1.7678
88	1.29	1.14	0.180	1.782	0.2511	1.9445	1.7678	

TABLE XVII

67	1.83	1.60	0.193	2.584	0.4123	1.8261	1.8367	
77	1.65	1.45	0.186	2.303	0.3623	1.8865	1.8337	1.8353
93	1.40	1.22	0.198	1.995	0.3000	1.9685	1.8354	

TABLE XVIII

67.5	1.62	1.43	0.180	2.237	0.3495	1.8293	1.7763	
77	1.40	1.22	0.198	1.995	0.3000	1.8865	1.7714	1.7745
93	1.25	1.10	0.184	1.738	0.2399	1.9685	1.7753	

TABLE XIX

67.5	1.87	1.70	0.137	2.389	0.3782	1.8293	1.8050	
76.5	1.66	1.50	0.146	2.156	0.3336	1.8837	1.8028	1.8044
93	1.42	1.28	0.149	1.854	0.2680	1.9685	1.8034	

TABLE XX

67.5	2.33	2.16	0.109	2.832	0.4521	1.8293	1.8789	
77	2.08	1.92	0.115	2.555	0.4074	1.8865	1.8793	1.8771
93	1.76	1.62	0.119	2.177	0.3379	1.9685	1.8733	

Tables IX–XII are illustrated graphically in Fig. 4. Tables IV–VIII and XIII–XX give graphs which are parallel to graph No. 9.

If the carbon black mixes be excluded, the effect of the addition of the com-

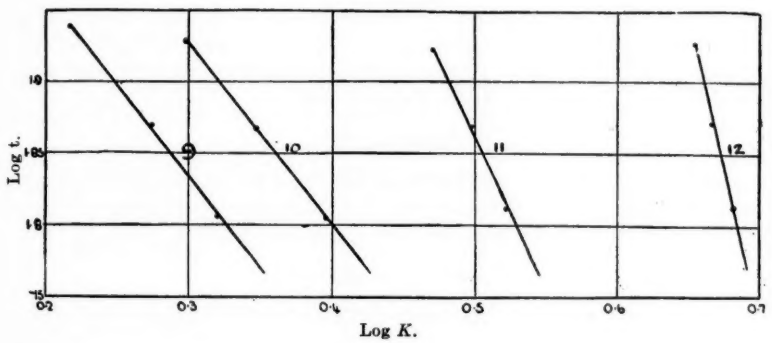

Figure 4

pounding ingredients examined is merely to alter the value of a, b being constant at 0.78. With carbon black, not only does a change, but also b for each addition of the material, both decreasing in value as the quantity of carbon black is increased. For any one mix a and b are constant at any one temperature.

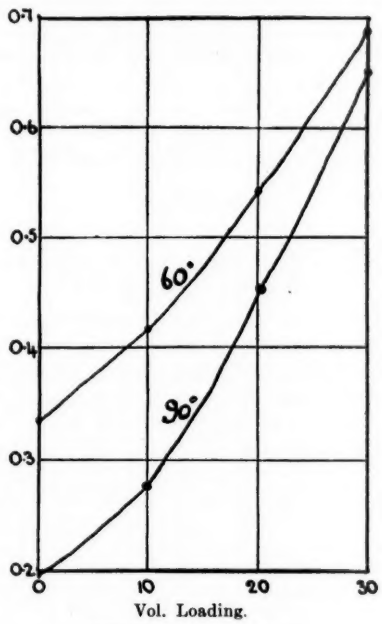

Figure 5—Carbon Black

Variation of Plasticity with Increasing Amount of Filler

The addition of 10 volumes of zinc oxide to 100 volumes of rubber produces a greater softening effect than the addition of 10 volumes of china clay. Ten volumes of carbon black, on the other hand, decreases the plasticity, *i. e.*, the value of K is increased. Further addition of zinc oxide caused toughening of the control rubber (Tables XVII and XX). Smaller quantities of zinc oxide than 10 volumes

produce softening of the control. Up to 20 volumes, china clay causes softening, but the addition of 20 volumes produces a relatively smaller softening effect than 15 volumes (Tables V–VIII). Carbon black stocks show a rapid rise in the value of K with increasing amounts of the material (Fig. 5).

Discussion

The data given show that, for the mixes examined and the range of temperature employed, the temperature and the value for the plasticity, represented by K, of rubber and rubber stocks are connected by the relationship:

$$\log K + b \log t = a$$

and, in general, a series of parallel straight lines is obtained if $\log K$ is plotted against $\log t$.

According to Williams, the index n in his formula for plasticity is a constant for the apparatus and the method of procedure. Griffiths (*Trans. Inst. Rubber Ind.*, 1, 325 (1925–26)), stated that the value of n was not constant but varied according to the rubber used from about 0.16 to 0.18. This variation in n has also been pointed out by Cotton (*Trans. Inst. Rubber Ind.*, **6**, 487 (1931)), who found values varying from 0.06 for tough rubbers to 0.3 for overmilled samples. It will be noticed in the present series of experiments that n not only varied with the rubber mix under test but also with the temperature for the same mix. It was a constant therefore for each sample at one temperature. The variations in the value of n appeared to follow no definite rule. In some cases, the value of n increased with increased temperature. In other cases it decreased or rose to a maximum and then decreased. The extreme values obtained during the present investigation were 0.215 (for a soft rubber) and 0.042 (for a hard mix).

Summary

1. A relationship of the type

$$\log K + b \log t = \text{a constant}$$

holds between the plasticity of rubber and rubber stocks and the temperature, where the plasticity is represented by Williams' equation $K = yx^n$.

2. In the case of soft mixes, b is constant and equal to 0.78, but in the case of harder mixes, *e. g.*, highly compounded carbon black stocks, the value of b is smaller in value.

3. The value of n in Williams' plasticity formula varies with the rubber and with the temperature.

[Reprinted from the Journal of Physical Chemistry, Vol. 36, No. 12, pages 2862–79, December, 1932.]

The Physical Structure of Elastic Colloids

W. F. Busse

PHYSICAL RESEARCH LABORATORY, THE B. F. GOODRICH CO., AKRON, OHIO

Introduction

Gelatin, rubber, polystyrene, polyesters, soap, chloroprene, etc., differ widely in chemical properties, but they have one outstanding physical property in common—under the proper condition their limits of elastic deformation are enormously higher than those of any similarly shaped crystalline material. Efforts to discover by chemical methods the cause of this high elasticity have not been particularly successful, though they have shown that linear polymers of sufficiently great molecular weights are often highly elastic. The attempts to find a physical explanation of the elasticity in some cases have been partially successful, but no thoroughly satisfactory theory is available.[1,9] The physical theories which have been proposed range from one which assumes the presence of tiny gas bubbles in the material to others which postulate a two-phase brushwork structure, or which assume the existence of helical molecules that act as tiny springs. Although some of these physical theories are satisfactory in limited fields, they usually are not valid for any wide range of materials, and difficulties are often encountered in applying them to a new field. This is illustrated by the attempt to account for the elasticity of rubber on the basis of the two-phase theory of the structure of gelatin gels.[8]

In this paper the mechanics of the process of elastic deformation is analyzed in the attempt to discover the fundamental general conditions which are necessary and sufficient to produce a high degree of elasticity in any material, and to formulate these factors as precisely as possible. The result is an explanation which appears to be more general and comprehensive than previous theories. It is shown that the factors which explain the high elasticity (*i. e.*, the great extensibility and recovery) will also account for other properties such as swelling in solvents, hysteresis, elastic after-effects, etc., which often accompany high elasticity. While specific chemical properties of individual systems are not considered in this analysis the theory of the physical factors responsible for elasticity is quite helpful in suggesting physico-chemical methods of modifying the properties of various elastic systems. One result of this study has been the production of fibrous and cellophane-like rubbers with rather unusual properties.

Concepts Included in the Term Molecule

In considering the structure of elastic colloidal materials, the gross physical properties are usually explained in terms of the properties of the primary units, or molecules. This, however, leads to confusion unless the various concepts included in the term molecule are clearly differentiated. An analysis of this term along the lines indicated by Bridgman[10] would be of great help in this field, and it is to be hoped that someone will carry it out.

For purposes of this discussion at least three concepts or three types of units which are more or less vaguely included in the term molecule are recognized. The

first is the chemical molecule, which is defined as the smallest unit possessing the chemical properties exhibited by a large mass of the material. In this sense the chemist requires the molecules of acetylene, benzene, acetic acid, and salt to be written C_2H_2, C_6H_6, CH_3COOH, and NaCl, respectively. These formulas are usually consistent with the common ideas of valence; organic chemists, therefore, sometimes define a molecule as a group of atoms held together by primary valence bonds. Under this latter definition, however, any perfect diamond must be regarded as a carbon molecule, and the so-called molecular compounds are excluded. For practical purposes—*i. e.*, for writing equations—the chemical molecules of solid elements such as iron, sodium, carbon, etc., are considered as single atoms, and the molecules of solid compounds are the smallest groups of atoms that possess the observed ratios of the elements in them, making the copper sulfate molecule $CuSO_4 \cdot 5H_2O$, the iron carbide molecule Fe_3C, etc.

A second concept included in the word molecule may be called the physical molecule. This unit will acquire from thermal vibrations an average of $^1/_2$ kT ergs of energy for each of three translational degrees of freedom, neglecting quantum restrictions. It is sometimes identical with the chemical molecule, especially in the gaseous state, and the chemist uses this concept of a molecule when he writes the molecules of common gases as H_2, N_2, O_2, Cl_2 and when he uses the weight, in grams, of 22.4 liters of a material in the gaseous state under standard conditions as the gram molecular weight. However, physical molecules also include such units as H, He_2^+, CH_3, which, though not very stable, can be recognized from band spectra; the particles of gold or mastic in colloidal solutions are also good examples of physical molecules. The sizes and weights of the physical molecules of a substance may change with temperature, rate of shear, and other factors, thus differing from the chemical molecules which, by definition, are invariants for a given substance.

When molecular weights are determined by cryoscopic or ebullioscopic methods, it is the average weight of the physical molecules which is obtained. When this weight is not consistent with the chemical formulas, special assumptions such as association, ionization, or solvation are made to explain the results, without always recognizing that several different concepts of molecules are involved. In general, the molecule of the organic chemist is both the physical and the chemical molecule, and cryoscopic methods may, therefore, be used to determine chemical molecular weights. If there is a discrepancy between the chemical and physical molecules, however, as in the case of acetic acid in a benzene solution, the organic chemist considers only the chemical molecules.

The distinction between physical and chemical molecules has been emphasized before, but the use of these concepts interchangeably still causes confusion in our thinking and discussions. This is particularly apparent in the field of colloids where the distinction between the two concepts is more important as well as more difficult to make, and because a third concept has crept into use which should be distinguished from the first two. When Einstein's equation is used to determine molecular weights by viscosity methods a third concept is introduced into the term molecule and in some cases a new unit is measured. This is a mechanical unit, the group of atoms which hold together when the material is subject to a shearing stress. To show its relation to the other units and to emphasize the broadness of the accepted usage of the term molecule, this unit will be called a "mechanical molecule."

The value of this concept is brought out in the case of compounds which form normal solutions in one solvent while in another they form gels even at very low concentrations. Viscosity measurements of these solutions do not reveal much

about the chemical molecules, though they may indicate the size of the mechanical molecules.

In gases and possibly in most liquids the physical and the mechanical molecules are identical; in liquids such as mercury, some of the mechanical molecules probably are also chemical molecules. In solids and in some colloidal solutions, where structures are built up through association forces, the physical and mechanical molecules may be quite different. When the units become very large, as in a macroscopic crystal or piece of a gel, the concept of the physical molecule becomes relatively unimportant, since the kinetic energy of translation acquired from thermal vibrations by a large particle plays only a small part in determining its properties. However, the larger the size of the units which hold together under a shearing force, the more important they are in determining the mechanical properties of a system. It is possible that in some cases the difference between the physical and mechanical molecule in a solid is merely a difference in point of view, but in other cases there seems to be a clear-cut physical distinction. In thixotropic systems such as vanadium pentoxide gels for example, the physical molecules of vanadium pentoxide may contain very large numbers of V_2O_5 particles. At very small shearing stresses the mechanical molecules may also be large groups of V_2O_5 particles, but at large shearing stresses the mechanical molecules may be the single V_2O_5 particles or micelles. The single water molecules, H_2O, as well as the polymers and perhaps the cybotactic groups[11] $(H_2O)_n$ are also mechanical molecules, the proportions of the different groups perhaps varying with temperature, rate of shear, etc.

The size of the mechanical molecule thus is not an invariant, as it changes not only with temperature, rate of shear, etc., but also, particularly in thixotropic systems, with the time of standing at rest. This is a part of the strength as well as the weakness of the concept; for, since it applies to a unit which can vary as conditions change, its use is not limited to infinitely dilute solutions or gases. The concept applies, for example, to gelatin or rubber solutions or from the most dilute (where the units of the solute which hold together during shear may be chemical molecules) to concentrated gels where association, thixotropy, etc., play important parts; it also applies to solids where the units held together by secondary forces may be more important than those held together by the primary valence forces.

The use of the concept of mechanical molecules makes it possible to avoid, for the time being, the problem of distinguishing between chemical molecules and micelles in dilute solutions, since from the standpoint of the mechanics of flow such a distinction is unnecessary. Likewise, the use of this concept clarifies other problems concerning the structure of solids, such as the question, "Is vulcanization a chemical or physical reaction?" by pointing out that it is the structure of the mechanical units which is important, whether these units are formed by physical or chemical means. It should be emphasized that our concepts are bound up with our methods of measurement and the concepts have value only when they are useful. In this paper the term molecule will be understood to be the mechanical molecule, except when it is specifically stated otherwise, since in most cases the chief interest is in the mechanical properties of the systems.

Ultimately there will probably be a quantum mechanics theory of molecular structure[12,13,14] which will make the above divisions obsolete. However, until then, when these limited concepts must be used, there should be an awareness of their defects as well as of their advantages.

The Structure of Elastic Colloids

The outstanding properties which must be explained by any satisfactory theory of the structure of elastic colloids are:

1. High elasticity—*i. e.*, large deformations which are followed by recovery to substantially the original size and shape upon removal of the deforming force.
2. Storing up free energy on deformation and the return of a large part of it as external work during the recovery.
3. Hysteresis.
4. Elastic after-effect, or slow recovery long (even days) after the deforming force is removed.
5. Swelling in suitable liquids, and sometimes dissolving to give solutions of high viscosity.

In addition, the theory should not be inconsistent with such specific properties as the Joule heat, x-ray fiber diagrams, etc. It should also account for the fact that many gels are elastic, though not all elastic bodies are gels.

The fact that elastic colloids can be deformed several hundred per cent and then recover to their original shape implies the existence of structural units in the material which also have this property. The unit cannot be the atom, for work on the strength of crystals[15] and metals,[16] on band spectra,[13] and on the Raman effect[17] has shown that a very great force is required to increase the distance between adjacent atoms in a molecule or crystal by as much as 30%, and rupture or plastic flow occurs at relatively low elongations. To make possible the elongations observed in elastic colloids, it is essential, then, to have some unit of mechanical structure made of groups of atoms to magnify the limited deformability of the single atoms. Many such structures have been proposed, but in most cases the authors have suggested molecular arrangements which are not common to all elastic colloids (helical rubber molecules, for example) or they have not clearly recognized the essential factors required to produce elastic structures (two-phase gel theories). An analysis of deformation processes indicates that the property of high elasticity requires, and is produced by, the following factors:

1. Groups of atoms which form strong, somewhat flexible fibrous units. These mechanical molecules may be physical or chemical molecules as well.
2. Weak or uniform cohesive (secondary valence) forces around the fibers.
3. An interlocking of the fibers at a few places along their length to form a three-dimensional network. This interlocking of the fibers may occur through chemical combination, by secondary valence forces, or by mechanical entanglements.
4. A means of storing up free energy in the fibers during deformation.

Evidence for the existence and importance of these conditions in elastic colloids will be given, and then it will be shown how these criteria of the necessary and sufficient conditions for high elasticity help to correlate and explain some of the specific physical properties of rubber.

1. *Long Fibers.*—The existence of a fibrous brushwork structure in two-phase gels is generally recognized. Such an arrangement is necessary to account for the fact that gels may be obtained containing only a few tenths of a per cent dry solid,[18] and that the rate of diffusion of molecules or ions through a gel differs only slightly from that in a sol of the same concentration.[21]

Usher and co-workers[19,20] found that during the gelation of a gamboge sol one could actually observe the particles line up into filaments which form a three-dimensional network, and they inferred that a similar structure existed in gels of cadmium sulfide and other lyophobic materials. They also found that the

viscosity of gas black and starch suspensions varied with the pressure only when there was a flocculated structure that could easily be broken up by small shearing forces. By means of a non-uniform dark field illumination, Szegvari[22] showed that the ultramicroscopic particles of V_2O_5 formed filament or needle shaped groups when the V_2O_5 sols set to a gel, and recent work on the dielectric constants of thixotropic systems indicates that the filament formation during gelation is due to the contact and adhesion of the solid particles to each other, rather than to any immobilizing of the surrounding liquid.[23]

Even in lyophilic gels, much of the liquid is mechanically entrapped in the interstices of some open structure rather than being bound by a chemical solvation, for one liquid in a gel can often be replaced by another of markedly different chemical properties without greatly changing its physical properties. The water in a gelatin gel, for example, may be replaced by organic liquids, or in some cases even by air.[24,25]

X-rays have shown that elastic materials which are not two-phase systems also contain fibrous units. Raw and vulcanized rubbers show an x-ray fiber diagram when stretched,[26] as do stretched dried gelatin[27] and synthetic linear high polymers, provided their molecular weights are great enough.[3,4,28,29] Solutions of these materials have high viscosities and show streaming double refraction.[30] For reasons discussed below a swelling agent must be used with some of these compounds to obtain high elasticity at ordinary temperatures.

While some sort of a fibrous mechanical structure is essential for high elasticity, the shape, stiffness, kinkiness, etc., of the fibers may vary widely among different systems. Nothing very definite is known about the precise shape of the fibers, other than that in materials like rubber, metastyrene, etc., the fibers are relatively thin and flexible—perhaps being only a single chemical molecule thick at most places—while in a fresh silica gel or a gamboge gel the fibers probably are many molecules thick and relatively stiff.

Purely geometrical considerations show, however, that the molecules of rubber do not have a helical shape, as has recently been proposed.[31,32] If the fibers are twisted so that consecutive double bonds are adjacent to each other across one turn of the helix the maximum elongation possible is about 300% or only about one-fourth that actually found in rubber. To make possible the observed elongations, they would have to be in the form of helixes containing 16 atoms of 4 double bonds to a turn. Such a shape would not be stable, however, due to the tendency of large ring compounds to assume irregular forms and to flatten out so that the opposite sides of the ring are adjacent to each other.[33]

Staudinger's assumption that in dilute solution the molecules of linear high polymers are practically straight, stiff elastic fibers does not seem reasonable in view of the possibility of rotation around single valence bonds, and this assumption is not necessary to explain his viscosity results. The most plausible hypothesis of the form of the rubber molecules in solution is that they are kinky fibers having a considerable range of lengths which mechanically entrap and practically immobilize a large volume of solvent.[34] This hypothesis is consistent with viscosity experiments carried on in this laboratory,[35] and with the collision areas of straight chain hydrocarbons calculated from the viscosity of their vapors.[36]

2. *Weak Cohesive or Secondary Valence Forces.*—Long fibrous units alone are not enough to produce elasticity. Parts of the fibers must be able to slide past each other without great difficulty if there are to be large deformations and recoveries. This implies weak or very uniform secondary valence forces around the greater part of each fiber, as well as implying a flexibility in the fibers themselves.

The weak secondary valence forces may be due to the arrangement of the atoms

and so may be a property inherent in the fibers themselves, as is probably the case in rubber. In other cases the fibers have relatively strong cohesive forces, but these can be effectively weakened or insulated by combining the fibers with small molecules which have much weaker secondary valence forces—in other words by swelling the fibrous material with a liquid having a low viscosity. Numerous examples of producing elasticity by this method are known—swelling gelatin with water or glycerine, cellulose esters with dibutyl phthalate, metastyrene with styrene, etc. In fact, this method of producing elasticity is so common that it has sometimes incorrectly been assumed that a two-phase gel structure was necessary for high elasticity.[8] It is not two phases that are necessary, however, but rather forces of two different orders of magnitude, strong forces along the fiber and weak forces around the fiber.

Another way of reducing the magnitude of the secondary valence forces is to increase the distance between the molecules by raising the temperature. Metastyrene and rubber hydrochloride are made elastic by this treatment, and cured rubber loses its elasticity when cooled to sufficiently low temperatures.[57] Moreover, Bridgman found that rubber lost its elasticity and was very hard under extreme pressures.

Whitby[4] recognized the importance of weak secondary valence forces when he attributed the slow recovery and what he called "the sub-permanent set" of elastic colloids to a high internal viscosity or an "elastic yield value." However, he states that the cohesive forces responsible for this "elastic yield value" are essentially the same as those responsible for the recovery of the materials after deformation, a view which does not entirely agree with that presented here. Von Weimarn[7] also pointed out that non-uniform "vectorial force fields" around molecules made it possible to bring them into a rubbery state, but he also assumed that a helical structure was necessary for elasticity.

3. *An Interlocking of the Fibers at a Few Places along Their Length.*—The high deformability of elastic bodies is not unique, for liquids and plastics are easily deformed. It is the high recovery of elastic colloids which puts them in a class apart. Shearing stresses can distort and orient long molecules in liquids as well as in solids, as shown by the phenomena of streaming double refraction,[30] etc. However, when the shearing stress is relieved in liquids the molecules quickly slide past each other and assume a random orientation without changing the external shape. In elastic solids the return of the fibers to their normal kinky forms makes the whole sample return to its original shape, showing that there is an interlocking and binding of the fibrous units at a few places along their length which prevents their slipping completely past each other.

The effective strength of the bonds holding the fibers together may vary within wide limits, consequently the range of conditions under which a sample will be elastic, (*i. e.*, will recover almost completely) will be very different for different materials. Some bonds may be weak enough to be broken by relatively small shearing forces as in the thixotropic ferric oxide sols studied by Schalek and Szegvari,[37] the weak gels formed in ammonium oleate solutions, or the flocculated gas black and starch suspensions studied by Usher.[20] In these cases the structure broken by the shearing stresses may again be re-formed on standing. Probably the forces which produce a thixotropic structure are similar to those causing the flocculation of pigments and the formation of crystals.[39]

In other cases the bonds between the fibers are stronger, formed, perhaps by a mechanical entangling of the fibers, aided by the weak cohesive forces around the fibers. The structure of raw rubber and metastyrene is probably of this type. As one would expect, raising the temperature increases the ease of untangling

the fibers, and these materials, therefore, show more slippage, or permanent set, at high temperatures.[38] Reducing the length of the fibers also reduces the chances of the fibers tangling, and it is found that milling raw rubber, which probably shortens the fibers by an oxidation process[40,41] greatly increases the flow or permanent set when it is subjected to a given force. While unvulcanized, dead-milled rubber flows readily under small forces applied for comparatively long times, it is nearly as elastic as cured rubber if the distorting force is applied for only a short time,[42] *i. e.*, if there is not sufficient time for the thermal vibrations to aid in untangling the molecules.

In vulcanized soft rubber there are much stronger bonds holding the fibers together so that flow and permanent set are small at room temperature, though they become appreciable at high temperatures or over long times.[43] This suggests that vulcanization involves a chemical union between different rubber molecules either through direct carbon to carbon bonds, or by means of sulfur (or Se, O_2, etc.) bridges.

The number of these bonds that exist in soft vulcanized rubber cannot be determined exactly, but some idea may be obtained of the upper and lower limits. The fact that vulcanized rubber can be elongated about 1000 per cent of its original length indicates that in this system the interlocking of fibers cannot be more frequent on an average than about one bond for every ten carbon atoms of the chain. This is the upper limit for the number of bonds, and the actual number probably is far less than this. The work of Bruni and Oberto[44] indicates that a minimum of 0.15% sulfur or one atom for each 315 C_5H_8 radicals is necessary for vulcanization, *i. e.*, to produce a noticeable change in the mechanical properties of rubber. Assuming one bond for each sulfur atom, this represents one bond for every 1260 carbon atoms of the chain, which is the extreme lower limit for the number of bonds necessary to affect the stress-strain curve appreciably. If it is assumed that vulcanized rubber is a chemically distinct material, and that two bonds are required for each original chemical molecule, these results indicate a molecular weight of the order of 20,000 for the particular sample of raw rubber which they used. If the theory of elastic deformation presented here is correct, the minimum sulfur required for vulcanization should increase with the amount of mastication of the rubber. One would also expect the amount of combined sulfur required for maximum strength to increase with the amount of mastication and these are found to be the facts.

Blake[45] reports that only 5.2% Se can combine with rubber in the soft rubber cure. If we assume that each Se atom forms a bond between two fibers, there would be a maximum of about one bond for every 23 isoprene groups, or one bond for every 92 carbon atoms in the chain, which, from mechanical considerations, is a reasonable figure.

The necessity for interlocking of the fibers of a gel at a few places along their length was recognized by Kistler,[24] who found that a cellophane aero-gel could be made with a volume 100% greater than the original cellophane, yet with nearly the same strength as the original. In the case of systems made of very flexible fibers such as rubber or gelatin, he could not produce an aero-gel. However, on stiffening the fibers, as on tanning a gelatin gel with formaldehyde, which increased the stiffness of the gel presumably by tying different fibers together with strong bonds, he was able to obtain a gelatin-aero gel.

4. *A Means of Storing Up Energy during the Distortion of the Fibers.*—Since elastic bodies can do work on retraction they must have a means of storing up free energy when they are distorted. This energy may in part be stored as potential energy in the fibers, because of a slight increase in the distance between adjacent

atoms in the fibers and through a distortion of the valence angles. This idea of a stiffness in the fibers is consistent with the concept of tetrahedral carbon atoms,[46] and it also agrees with the new wave mechanics.[47,48] It does not follow, however, that the fibers are even approximately straight rods, or that they have the zig-zag shape attributed to fatty acid molecules closely packed on the surface of water. In long molecules, the thermal vibrations instead of causing the molecules to vibrate as thin glass fibers might easily cause rotation around single valence bonds to produce a very kinky shape. Haller[6] has calculated, on the basis of Raman spectra data for the energy required to deform valence angles, that if the molecules vibrated as rods, the average bending of a paraffin hydrocarbon chain of 100 carbon atoms would be an angle of about 16.4°, while a chain of 10,000 carbon atoms would be bent, on the average, 163.5° from a straight line. It follows from purely geometrical reasons that thermal vibrations will have a strong tendency to restore a kinky shape to long fibrous molecules after they have been straightened by an external force.[49] Probably at all times there will be a rapid interchange of potential and kinetic energy due to thermal vibrations.

When the fibers are in nearly parallel alignment the effect of thermal vibration in causing contraction may be more than counterbalanced by the tendency of the molecules to form crystalline units with evolution of heat. This is exhibited as racking and as the Joule heat in rubber, and similar effects are observed in chloroprene.[28] Such an effect can be expected only when there is a uniform periodicity in the intensity of the secondary valence forces such as would be obtained when the fibers are made by repeating some simple unit.

If the recovery of elastic colloids is due to the potential energy stored in the distorted atoms and to the effect of thermal vibrations, the elasticity of chemically saturated materials such as gelatin, metastyrene, etc., and of unsaturated ones such as rubber, may be explained on the same basis. It is not necessary then to account for the elasticity of rubber on the basis of the attraction of double bonds across the turns of the helix.[26,50] Nor is this helical structure necessary to account for the S-shape of the stress-strain curve of rubber; for if the stress-strain curve of rubber is calculated on the basis of the instantaneous cross sections of the sample, it is not S-shaped.[51,52]

This stiffness of the fibers also accounts for the swelling pressure of gels. If the fibers are in the normal random kinky shape when a gel such as gelatin is formed in solution, the fibers on drying will be distorted as the gel contracts in size because of the capillary and cohesive forces. After the liquid is evaporated, the cohesion between the separate fibers is great enough to keep them in their distorted positions, in spite of the thermal vibrations which tend to relieve strains at the valence angles. On again putting the gel in water, the cohesive (or secondary valence) forces around the molecules will be satisfied by the smaller water molecules, and the fibers can then untangle so as to relieve the distortion as much as possible.

The swelling of a gel, then, consists of two parts. The first is an adsorption of the swelling liquid on the gel fibers by means of the secondary valence forces which may involve a liberation of heat. The adsorbed layer effectively insulates these secondary valence forces, thus allowing the fibers to move past each other and assume a random kinky shape with the minimum average distortion of the valence angles. This latter part of the expansion may involve an absorption of heat, even though there is a decrease in free energy.

As the swelling continues new positions of strain may be introduced into the molecules and these may finally balance any further tendency to swell. This limited swelling occurs only when the molecules are long enough to be quite firmly tangled or snarled, or when there is a combination of molecules through very strong

forces (polymerization, etc.) to make the sample a mechanical unit, as probably is the case in cured rubber. This effect also appears in gelatin gels which have been formed from solutions of different concentrations. The amount of water they will again take up after drying will be found to depend on the concentration at which the gel was formed, the gels formed from dilute sols taking up more water than gels from concentrated sols.[53] The contacts made at the time the gel is formed determine the amount of swelling that will produce the minimum distortion of the valence angles. The anistropic swelling of gelatin gels observed by Sheppard and McNally[54] also shows that there are strains in the dry gels determined by the conditions under which the gels are formed and dried.

This theory of the cause of the swelling pressure gives a very simple explanation of the results of Stamberger and Blow,[55] who found that a given concentration of raw rubber produced the same swelling pressure as dead-milled rubber, though one was a swollen gel and the other a relatively mobile liquid. The effect produced by the tangled molecules trying to expand and minimize the distortion of the valence angles may be visualized as being somewhat similar to the effect produced when a number of tennis balls is placed in a cylinder and compressed by a piston. The balls will exert a given pressure when compressed a definite amount by the piston, and on removing the piston the balls can be poured out of the cylinder. If, however, the balls are coated with an adhesive and then packed into the cylinder in the same way and the adhesive allowed to dry, the balls will be fastened together wherever they come into contact in their undeformed state. The balls will exert the same pressure as before when compressed by the piston, and on removing the piston the group of balls will regain its original shape, but the individual balls cannot be poured out of the cylinder. Similar results would be obtained if the molecules were considered as tangled springs instead of tennis balls. If this picture is correct, and the swelling pressure is independent of molecular size, it follows that in concentrated solutions, where swelling pressures can be measured, and for compressive stresses, such as are applied in measuring swelling pressures, the volume occupied by the mechanical molecules is proportional to their weight. This relation is very different from the results found by Staudinger[1] and Fikentscher and Mark[50] for dilute solutions, but it is consistent with the view that in solids and concentrated gels the molecules have a more or less compact kinky shape.

Since this paper was presented, a paper by Meyer, von Susich, and Valko[70] has appeared in which they abandon the idea of a helical rubber molecule, and conclude that one must avoid the use of models if he is to get a fundamental understanding of the mechanism of elastic deformation. The kinetic theory of elasticity which they present emphasizes the factor of thermal vibrations of groups of atoms within the molecule, and is consistent with the theory given above.

Application of Theory to Specific Properties of Rubber

This theory is of value in interpreting and correlating many of the specific physical properties of elastic systems. In the case of rubber, for example, the theory does not tell anything about the proper accelerators of vulcanization to be used to produce definite properties such as low permanent set, or low hysteresis, or high elongations. However, accepting the view that raw rubber consists of long, kinky, fibrous molecules, and that soft rubber vulcanization produces strong (presumably chemical) bonds between the molecules of crude rubber, one would expect, and actually finds, the following physical properties accompanying those already considered.

1. *Creep and Elastic After-Effect.*—Even with relatively weak cohesive forces around the fibers one would expect that any large elongation or recovery would

cause the kinky fibers to move so far that some parts would become jammed or tangled up in intermediate equilibrium positions. The energy of thermal vibrations would then cause the jammed groups of atoms, or parts of fibers, to escape slowly from these temporary equilibrium positions and become at least partly untangled. This produces a slow creep after the initial rapid elongation, when the sample is stretched by a constant load. If the rubber is stretched to a constant elongation, this untangling will be manifested as a slow decrease in the stress.

When a stretched sample of rubber retracts, groups of atoms again have to move considerable distances past other rubber molecules, and there is as much chance of these groups jamming in intermediate equilibrium positions as there was during the stretching. These tangles are undone only when the energies of the thermal vibration are great enough to move the groups out of the intermediate equilibrium positions. The resultant continued retraction is the elastic after-effect.

A mathematical treatment of this process is very difficult, and only by making some rather improbable assumptions was it possible to derive relations between length and time which approximately fit the experimental results. Phillips,[56] found that the increase in the length on stretching for vulcanized rubber was given by the formula:

$$E = a + b \log t$$

where E is the increase in length, t is the time, a and b are constants. For unvulcanized rubber the formula was of the type:

$$\log E = a + b \log t$$

Work in this laboratory has indicated that the latter formula is valid for certain kinds of vulcanized rubber, also.

This explanation of the elastic after-effect, of course, is analogous to the explanation of the slowness of many chemical reactions. A knowledge of the temperature coefficient of this process (measured without complicating side effects) would permit the calculation of the average amount of energy that must be added to a molecule or part of a molecule to remove it from these intermediate equilibrium configurations, or jams, just as a knowledge of the temperature coefficients of chemical reactions makes it possible to calculate the heats of activation.

Elastic after-effects may be produced by the tendency to form fibrous crystals, as well as by the mechanical jamming of the fibers. The racking of raw rubber is an extreme example of this effect. Here the slowness of the retraction is due to time required for the sample to acquire from the outside the heat necessary to melt the crystals, so it might be called a thermal elastic after-effect. Both types of elastic after-effects are reduced by raising the temperature. On lowering the temperature there should be more tangling of the fibers and the rate of disentangling should decrease, due to the greater magnitude of the cohesive forces around the fibers, causing the modulus of rubber to increase as the temperature is lowered, as was found by Mark and Valko[57] and by Rosbaud and Schmid.[58]

It may be mentioned that no elastic after-effect other than that due to thermal, electrical, or other secondary thermodynamic effects can occur in a perfect crystal.[59] An elastic after-effect produced by shearing forces requires the existence within the sample of groups of atoms held together by strong forces and surrounded by weak forces.

The mechanism of the jamming of large groups of atoms during deformation and recovery suggested above leads one to expect that rubber will exhibit a higher modulus—that is, a lower elongation for a given force—if the force is applied

quickly rather than slowly; this actually occurs. Further evidence for the jamming and tangling of the molecules on distortion is found in the experiments of Prache.[60] On loading a sample of raw rubber with a 400-gram weight he obtained a certain elongation. On reducing the weight to 100 grams the sample contracted to a length less than it would have had if this 100-gram weight had been applied originally. After this contraction the sample then slowly stretched to its normal length under a 100-gram load. The stretching under the 400-gram weight evidently was more rapid than it would have been with a 100-gram load, so there was more jamming of groups in intermediate positions, making the sample stiffer, and causing a larger contraction upon removal of the weight. Rearrangement and untangling of these jammed groups then permitted the sample to further elongate to its normal length when stretched by a 100-gram weight. A similar result was obtained by Mr. Davies of this laboratory by compressing samples of uncured rubber under different weights in the Goodrich plastometer.[61]

3. *Permanent Set.*—If the sample does not completely recover from a deformation it is said to have acquired a set. It is important to distinguish between two very different conditions which may produce this effect. The first is a true permanent set, produced when the fibrous molecules are not firmly interlocked. In this case the molecules may relax by sliding completely past each other. This is simply a viscous or plastic flow which reduces the strain in the molecule without changing the external shape of the sample. If this action is carried to the limit the sample becomes isotropic. Anything which will decrease the binding between the fibers, such as raising the temperature, swelling with solvents, etc., will increase the permanent set produced by this cause; reducing the length of the molecules will have the same effect. Milled rubber acquires a greater permanent set than unmilled rubber and the permanent set is lowest for the highest members of a homologous series of polymers.

The second cause of permanent set is essentially a very slow elastic after-effect, usually a thermal elastic after-effect as in racked raw rubber. If the temperature is lowered far enough, cured rubber will show a similar effect, for at the lower temperature the balance between the cohesive forces, thermal vibrations, and strains at the valence angles is changed so the molecules no longer can contract. Whitby called this slow elastic after-effect the "sub-permanent set." Raising the temperature or adding solvents to rubber will reduce this type of elastic after-effect.

It follows from this mechanism that not only will the modulus of the rubber increase, but the permanent set will decrease when the speed of deformation increases. The elastic recovery of raw milled rubber is nearly as great as that of cured rubber if the time of deformation is small. This can be demonstrated by bouncing balls made of cured rubber and milled raw rubber. They will bounce to nearly the same height, although they have very different values for stiffness and permanent set when the loads are applied for longer times.[42] In a rapid deformation cycle, the mechanical tangling and jamming of the molecules is sufficient to keep them from flowing, even though there are no strong chemical bonds holding the fibers together. There is not enough time for thermal vibration to aid in getting the molecules out of the intermediate equilibrium positions or to flow. The sample, therefore, shows a high recovery.

4. *Hysteresis.*—For a minimum hysteresis in a sample of rubber which is subjected to mechanical distortion, it is necessary to reduce to a minimum the slow creep and elastic after-effects as well as the plastic flow. Such a result would be accomplished if there were a weak binding force or attraction between the molecules permitting them to slide past one another easily everywhere except at the few points where there is the strong interlocking necessary to prevent plastic

flow. This condition may be realized if rubber is swollen with a large amount of oil and then vulcanized. The quivering of a cured cement, for example, shows that its hysteresis actually is very low, at least for small deformations.

The hysteresis due to the tangling and untangling of the molecules may be reduced by going through the deformation cycle either very rapidly or very slowly, provided the permanent set is low. In the first case there will be a great deal of tangling. However, since there is little time for the fibers to become untangled the sample will exert nearly the same force during the recovery as it does during the stretching. In the second case, when the rate of stretching and recovery is very slow the thermal vibrations enable the fibers to take up equilibrium positions during both the stretching and recovery, so the hysteresis loop is small if there is no permanent set.

Another method of reducing hysteresis and securing equilibrium stress-strain curves is to help the molecules out of the jams by making the sample oscillate during the stretching. Stress-strain curves of this type were obtained by Gerke.[62] One would expect from thermodynamic considerations that the modulus of the rubber would be somewhat greater at high temperature than at low temperature for the stress-strain curves obtained in this way, and the limited data reported by Gerke indicated that such may be the case. His results also showed that time of cure has no effect on the equilibrium stress-strain curve and he cited this as evidence that the curing of rubber affects the plastic properties of rubber more than the elastic properties; Williams[42] reached a similar conclusion from the study of stress-strain curves at high speeds. It is evident that cure influences the elastic after-effect and creep as well as the plastic flow, and these are parts of the elastic properties of rubber.

This analysis of the deformation of rubber differs considerably from that of Ariano[63] who postulated a "point of viscous diffusion," "plastic state," and "liquid viscous state" between the solid and liquid states to explain the observed elastic properties. As a real explanation of the behavior of rubber under mechanical distortion, the molecular mechanism suggested above seems greatly preferable to naming hypothetical states between idealized solid and liquid states.

5. *Other Physical Properties.*—The optical properties sometimes give considerable information about the chemical as well as the physical structure of materials. Recent work on the Raman spectra provides a very convenient method for studying the infra-red absorption spectra of various materials, and it was thought that this line of attack might show something about the structure of rubber and similar hydrocarbons. Preliminary experiments were carried out by Professor Williams and Mr. Hollaender at the University of Wisconsin, to see if the Raman spectra of rubber, gutta-percha, and balata in carbon tetrachloride solutions showed any distinctive differences. Since the materials were all carefully purified they darkened readily through oxidation on exposure to air. This made it difficult to obtain the Raman spectra. On exposure to a mercury arc, however, the gutta-percha solution showed a few Raman lines around 4600 Å, probably excited by the mercury line 4359 Å, and a broad band around 4780 Å. Pale crepe and balata showed similar bands. Others have also found broad bands in studying the Raman effect of rubber solutions.[64] The fact that bands rather than lines are obtained may be due to the high viscosity of the solution, or it may indicate that the rubber groups can respond to a wide range of frequencies. It was found in this work that all the solutions gelled on the side exposed to the light, although they were in pyrex glass vessels which transmit only down to a wavelength of 3200 Å. This gel structure formed in gutta-percha and balata as well as in rubber. It probably is not identical with that produced by vulcanization

with sulfur or sulfur chloride, but at least it involves the linking together, by rather strong bonds, of units which previously were separated.

The tendency of kinky fiber molecules to expand and relieve the internal stresses accounts for the swelling pressure and the mechanical entrapping of liquids by gels, and it also implies that a similar mechanical entrapping of solvent should occur in solutions. Work done in this laboratory[35] several years ago on the temperature coefficient of the viscosity of rubber solutions supports the view that their high viscosity is due to this cause.

Dunn,[65] Andrade,[66] and others have shown that the change of viscosity with temperature of non-associated liquids can be represented by an equation of the type $\log 1/\eta = A/T + B$, where η is the viscosity, T the absolute temperature, and A and B are constants. By assuming that the fluidity $(1/\eta)$ is a measure of the rate at which molecules acquire sufficient energy q to leave their transient equilibrium positions (cybotactic state[11]), the writer derived the above relation between fluidity and temperature in the form $1/\eta = CS^{r-1}e^{-q/kT}$, where S is the shearing stress, C and r are constants, and the other terms have their usual significance. This equation includes the relation between shear and fluidity found by Nutting. The validity of this interpretation of viscosity is confirmed by data recently published showing the relation of viscosity to the perfection of orientation for 22 octyl alcohols.[67] The changes in the constants C and q, or A and B can, therefore, be interpreted in terms of changes in the structure of the solutions. Tests on rubber solutions in several solvents and over a wide range of temperature and concentrations showed that the value of q in pure solvents differed only slightly from the values in rubber solutions, provided they were not too concentrated. If there were an adsorptive binding of the solvent to the rubber molecules such as was assumed by Fikentscher and Mark,[50] one would not expect this result, so it is probable that the binding of the solvent molecules is largely a mechanical entangling.

6. *Cured Racked Rubber.*—Fibrous rubber has been produced in various ways: racked rubber which has been cooled to liquid air temperatures can be shattered to show a fibrous structure; Kirchhof[68] and Mark and Susich[69] obtained fibrous materials by allowing racked rubber to react with sulfuric acid, chlorine, bromine, and iodine at low temperatures for periods up to several months. Mechanically fibrous materials were obtained in every case, but the bromine treated rubber did not give an x-ray fiber diagram. All these materials were relatively weak or brittle and did not have any remarkable physical properties.

From the above theory of rubber structure, it was thought that vulcanizing rubber destroys its ability to become racked for one of two reasons. If during vulcanization random bonds are introduced between the fibers this will cause additional strains and distortions when the fibers are arranged parallel to one another by an external force, and the additional strains will prevent the secondary valence forces from holding the fibers in position except at very low temperatures. It is also possible that the chemical reaction during cure changes the intensity and distribution of the secondary valence forces so that the fibers cannot be made parallel, or else the forces are not strong enough to hold them parallel if they are oriented by an external force. In either case one would expect to obtain a rather interesting product if the rubber were first racked and then cured. Attempts to cure racked rubber with sulfur and ultra-accelerators at room temperature or slightly above usually resulted in producing what was in effect merely a cured rubber with a strong calender grain.

When racked rubber was cured in a stream of dry sulfur chloride vapor, a strong, horny, fibrous product was obtained with rather unusual properties. It was found

that the tensile strength of the samples depended greatly upon the elongation previous to cure, just as the strength of rubber at very low temperatures depends on the elongation of the sample before cooling.[57] In one case sheets of evaporated latex 0.005-inch thick were cured in a stream of dry sulfur chloride vapor for 15 min. at 0° C., after being racked different amounts. The tensile strengths varied from about 200 to 17,000 lbs. per sq. in., as shown in the following table:

Initial Stretch (Per Cent)	Tensile Properties of Cured Sample	
	Ultimate Elongation (Per Cent)	Tensile Strength (Lbs. per Sq. In.)
0	15	220
300	20	4560
600	20	7070
900	30	10,450
1200	25	17,100

Similar results have been obtained at room temperature or even higher, over a wide range of curing times. If the samples are very thick only the surface is cured leaving the inside still uncured even after several hours, and the samples are relatively weak and brittle. It is probable that the tensile strengths shown in the above table are not the maximum that can be produced, and it is likely that rubber fibers can be prepared with a strength comparable to the best textile fibers. Samples of cured racked rubber gave sharp x-ray fiber diagrams.

The fibrous product is cured to the hard rubber stage by the sulfur chloride. In one case a 30-minute cure gave a material containing 15.2 per cent sulfur, while the compound $(C_{10}H_{16})_2S_2Cl_2$ requires 15.7 per cent sulfur. The cured racked rubber may be left in sulfur chloride vapor up to 15 hours without noticeably changing its tensile properties, although the unstretched rubber becomes very brittle when left in the vapor for fifteen minutes.

From the point of view of the mechanical structure of rubber presented here one would expect that fibers could be obtained by stretching cured soft rubber and further curing it in sulfur chloride vapor while stretched. This was tried, using a rubber-sulfur mixture and accelerated stocks, and fibrous rubbers were obtained in every case. However, the accelerators, zinc oxide, age resisters, and other compounding ingredients made it necessary to increase the time of cure, and the final product was not quite as good as that obtained with crude unmilled rubber. This may have been because the cured rubber could not be elongated as much as the evaporated latex.

If the rubber is stretched in two directions at once and then cured, a very interesting non-fibrous parchment-like material is obtained. In this case the molecules probably are stretched out into fibers which are oriented at random in a plane. The product is quite strong and flexible in thin sheets, and is very resistant to organic liquids, even boiling toluene does not change it appreciably.

Summary

1. Some of the concepts included in the term "molecule" are briefly discussed and it is pointed out that the mechanical molecule is often the most important one in colloid systems.

2. The elastic properties of colloid systems require, and are produced by a group of four factors:

(a) Long fibrous molecules.
(b) Weak or uniform cohesive forces around the fibers.

(*c*) An interlocking of the fibers.
(*d*) A means of storing up free energy when the fibers are distorted.

3. Evidence for the existence of these factors in elastic colloids is discussed and is applied to account for and correlate some of their physical properties.

4. The theory of the structure of elastic colloids presented here has suggested means of preparing fibrous and parchment-like rubbers having rather unusual properties.

References

[1] Staudinger, *Ber.*, **62**, 2893 (1929); *Kolloid Z.*, **53**, 19 (1930).
[2] Meyer and Mark, "*Der Aufbau der hochpolymeren Substanzen*," **1930.**
[3] Carothers, *Chem. Rev.*, **8**, 353 (1931).
[4] Whitby, *J. Phys. Chem.*, **36**, 198 (1932).
[5] Herzog, *Kolloid Z.*, **53**, 46 (1930).
[6] Haller, *Kolloid Z.*, **56**, 257 (1931).
[7] Von Weimarn, Alexander's "Colloid Chemistry," **3**, 89 (1931).
[8] Bary and Hauser, *Rev. gén. caoutchouc*, **5**, No. 42, 3 (1928); *Rubber Age* (N. Y.), **23**, 685 (1928). This contains a good summary of early theories of the structure of rubber.
[9] Freundlich, "Colloid and Capillary Chemistry," **1926.**
[10] "Logic of Modern Physics," **1927.**
[11] Stewart, *Rev. Modern Phys.*, **2**, 116 (1930).
[12] Heitler, *Z. Physik*, **31**, 185 (1930).
[13] Mulliken, *Chem. Rev.*, **9**, 347 (1931); *Rev. Modern Phys.*, **4**, 1 (1932).
[14] Pauling, *Chem. Rev.*, **5**, 173 (1928).
[15] Joffé, "Physics of Crystals," **1928.**
[16] Mehl, *J. Am. Chem. Soc.*, **52**, 534 (1930).
[17] Andrews, Phys. Rev., [2], **35**, 662 (1930).
[18] Holmes and Maxson, *Colloid Symposium Monograph*, **5**, 287 (1928).
[19] Usher, *Proc. Roy. Soc.*, **125A**, 143 (1929).
[20] McDowell and Usher, *Proc. Roy. Soc.*, **131A**, 409 (1931).
[21] Reference 9, p. 727.
[22] Szegvari, *Z. Physik*, **21**, 348 (1924).
[23] Kistler, *J. Phys. Chem.*, **35**, 815 (1931); Kallman and Kreidl, *Z. physik. Chem.*, **159A**, 322 (1932).
[24] Kistler, *J. Phys. Chem.*, **36**, 52 (1932).
[25] Erbring, *Kolloid Z.*, **57**, 195 (1931).
[26] Meyer and Mark, *Ber.*, **61**, 1939 (1928).
[27] Katz and Gerngross, *Naturwissenschaften*, **13**, 900 (1925); Gerngross and Katz, *Kolloid Z.*, **39**, 181 (1926).
[28] Carothers, Williams, Collins, and Kirby, *J. Am. Chem. Soc.*, **53**, 4203 (1931).
[29] Carothers and Hill, *J. Am. Chem. Soc.*, **54**, 1566, 1579 (1932).
[30] Signer, *Z. physik. Chem.*, **150A**, 257 (1930).
[31] Kirchhof, *Kautschuk*, **6**, 31 (1930).
[32] Fikentscher and Mark, *Kautschuk*, **6**, 2 (1930).
[33] Reference 3, p. 378.
[34] Haller, *Kolloid Z.*, **56**, 17 (1931).
[35] Busse and Karrer, "The Application of Dunn's Viscosity Equation to Rubber Solutions," Atlantic City Meeting of the American Chemical Society, September, 1929.
[36] Melavan and Mack, *J. Am. Chem. Soc.*, **54**, 888 (1932).
[37] *Kolloid Z.*, **32**, 318 (1923).
[38] Dieterich, *Ind. Eng. Chem.*, **21**, 768 (1929).
[39] Jong, *Kolloidchem.-Veihefte*, **29**, 454 (1929).
[40] Cotton, *Trans. Inst. Rubber Ind.*, **6**, 487 (1931).
[41] Busse, *Ind. Eng. Chem.*, **24**, 140 (1932).
[42] Williams, *Ind. Eng. Chem.*, **21**, 872 (1929).
[43] Van Rossem and van der Meyden, *Rubber Age* (N. Y.), **23**, 438 (1928).
[44] *Rev. gén. caoutchouc*, **8**, No. 75, 19 (1931).
[45] *Ind. Eng. Chem.*, **22**, 744 (1930).
[46] Kettering, Shutts, and Andrews, *Phys. Rev.*, [2], **36**, 531 (1930).
[47] Slater, *Phys. Rev.*, [2], **37**, 481 (1931).
[48] Pauling, *J. Am. Chem. Soc.*, **54**, 988 (1932).
[49] Karrer, *Phys. Rev.*, [2], **39**, 857 (1932).

[50] Fikentscher and Mark, *Kolloid Z.*, **49**, 135 (1929).
[51] Hatschek, *J. Soc. Chem. Ind.*, **40**, 251T (1921).
[52] Ariano, *India Rubber J.*, **72**, 271 (1926).
[53] Reference 9, p. 209.
[54] Sheppard and McNally, *Colloid Symposium Monograph*, **7**, 17 (1929).
[55] Stamberger and Blow, *Kautschuk*, **6**, 22 (1930).
[56] *Phys. Soc. London*, January 29, 1905.
[57] *Rev. gén. caoutchouc*, **7**, No. 64, 11 (1930).
[58] *Z. tech. Physik*, **9**, 98 (1928).
[59] Reference 15, p. 23.
[60] *Caoutchouc and Gutta Percha*, **1930**, 15003.
[61] Karrer, Davies, and Dieterich, *Ind. Eng. Chem., Anal. Ed.*, **2**, 96 (1930).
[62] *Ind. Eng. Chem.*, **22**, 73 (1930).
[63] *Nuovo Cimento*, March, **1929**; *India Rubber J.*, **78**, 316 (1929).
[64] Franklin and Laird, *Phys. Rev.*, [2], **36**, 147 (1930).
[65] *Trans. Faraday Soc.*, **22**, 401 (1926).
[66] *Nature*, **125**, 582 (1930).
[67] Stewart and Edwards, *Phys. Rev.*, [2], **38**, 1575 (1931).
[68] *Kautschuk*, **5**, 9 (1929).
[69] *Kolloid Z.*, **46**, 11 (1928).
[70] Meyer, von Susich and Valko, *Kolloid Z.*, **59**, 208 (1932).

[Translated for Rubber Chemistry and Technology from Kautschuck, Vol. 9, No. 9, Pages 130–134, September, 1933.]

The Resistance of Anisotropic Rubber Sheets to Cutting and to Tearing

F. Kirchhof

HARBURG, GERMANY

The interesting experiments of Talalay[1] on the resistance of rubber mixtures to cutting suggested to the present author that it might be fitting to describe certain observations of his own, made at the same time, on the behavior of rubber mixtures prepared from latex. Since in the preparation of such mixtures all mastication of

A *B* *C* *D*

Figure 1—Demonstration of the Resistance to Cutting and and to Tearing of Unbroken Films of Jatex Rubber-Shellac Mixtures

A. Cuts and tears in untreated films
B. Film stretched to 100 per cent and released before tearing. Residual elongation 10 per cent.
C. Released film warmed to 80° C. for a brief time before tearing in order to contract the deformed latex particles.
D. Cuts and tears perpendicular to the direction of stretching.
The marks *e* represent cuts preliminary to tearing.

the rubber is avoided, the relations are simpler than in the case of masticated rubber mixtures, and a better insight into the nature of the physical properties of the former is certain to be obtained.

In addition to these experiments, the measurement of the resistance to tearing of calendered, vulcanized rubber sheets is discussed.

Observations on the Resistance of Unvulcanized Latex Films to Cutting, and the Effect upon This Resistance of Mechanical Treatment of the Films

In connection with experiments with latex mixtures, films were prepared by evaporation and drying at 55° C. of Jatex[2] mixtures containing about twenty per cent of shellac resin, which had been added to the Jatex in the form of a solution of its ammonium resin soaps. These films, which were about one millimeter thick, were dark brown and transparent, but upon stretching to two or three times their length became light brown and opaque.

Although before mechanical treatment, the films showed considerable resistance in all directions to tearing after cutting, and ultimately tore in a crescent-shaped manner, films which had been stretched two or three times to 100–200 per cent of their length and released showed, after being notched in the direction of stretching, a tendency to tear in the same longitudinal direction when the torn ends were pulled apart (see Fig. 1, A and B). The stress necessary to continue the tearing in the direction that the film had been stretched was considerably less than the stress necessary to tear at right angles to this direction. The elongated films showed permanent elongations of 10–15 per cent of their original lengths.

A similar behavior upon continued tearing was shown by films which after stretching had been warmed to 80° C. for a short time to eliminate their residual elongation. Here too, tearing was very easy in the direction of the original elongation, whereas at right angles to this direction the tears were again of a crescent form (Fig. 1, C and D).

In contrast to this latter behavior, Jatex films containing no shellac, but which had been strongly racked and contracted by warming, showed no more tendency to tear in the direction of stretching than at right angles to this direction, while in the racked condition a ready separation into fibers in the direction of racking was observed, as described earlier by Feuchter.[3] In the films containing shellac there must therefore be a partial fixation, by aid of the colloidal shellac-resin particles, of the rubber particles in the position in which they have been deformed by stretching. This in turn leads to the phenomena observed during milling and calendering of rubber mixtures, *i. e.*, calender effect and grain.

TABLE I

RESISTANCE TO CUTTING AND TO TEARING OF JATEX RUBBER FILMS CONTAINING 20 PER CENT OF SHELLAC, AT 15° C.

Sample	Thickness of Film in Mm.	Resistance to Cutting (C) and to Tearing (T) in Grams	
		Experimental Value	Calculated to a Basis of 1 Mm. Thickness
(a) Original film, unstretched	1.5	670 (C)	446 (C)
(b) Original film, unstretched but at right angles to the preceding direction	1.5	675 (C)	450 (C)
(c) Film unstretched, but warmed to 80° C.	1.0	450 (C)	450 (C)
(d) Film stretched to 200 per cent and released	0.6	170 (T)	280 (T)
(e) The same	0.65	190 (T)	290 (T)
(f) Film stretched to 200 per cent and released, but in a direction at right angles to that of the previous sample	1.3	620 (C)	477 (C)

It is suggested that the resistance of a one-directional anisotropic rubber sheet to further tearing in this direction be distinguished from its resistance to cutting

by characterizing the former as the resistance to separation, which is somewhat analogous to the greater tendency of fabrics to tear in the warp or weft direction. This resistance to separation can be expressed in grams per millimeter of thickness.

The measurements of the resistance to cutting and to tearing of the unstretched and of the stretched Jatex rubber films containing shellac are given in the foregoing table:

These results in Table I show that the anisotropy brought about by stretching was accompanied by a considerable loss in resistance to cutting in the direction of stretching. In contrast to the unstretched films, this lowering of the resistance was about 40 per cent. On the contrary at right angles to the direction of stretching, there was a slight toughening, which was evident in an increased resistance to cutting.

The anisotropy described above, and which is brought about by stretching, is also manifest in an x-ray diagram.[4] Whereas the unstretched rubber film containing 20 per cent of shellac showed only an amorphous ring and the stretched film an almost ideal fiber structure, the film which had been stretched to approximately 200 per cent and released showed an incomplete fiber orientation. In this latter condition, the rubber was partially crystalline, but the position of the crystallites varied to a considerable extent with the direction of stretching (fiber axis). The weak fiber diagram can be accounted for only by the rubber crystallites which had been oriented by the stretching and had been partially fixed in position by the shellac resin particles. The tendency of the films to become opaque or transparent during and after stretching is to be ascribed in all cases to the fact that the colloid shellac resin particles which were adsorbed on the surface of the latex particles in the undisturbed film partially coagulated, as a result of pressure and frictional forces during stretching. This led in turn to a change in the optical properties, *i. e.*, in the refractive index.

Jatex-shellac films obtained by evaporation, and therefore without any original external influence on the structure, showed certain other noteworthy characteristics which depended upon the reënforcing and stiffening effects of the highly dispersed shellac resin phase.

An idea of the marked reënforcing effect of colloidal shellac-resin particles may be had by stressing to the point of rupture films which had previously been stretched to 3.5 times their original length, *i. e.*, to the break in their stress-strain curves. In this case a permanent elongation of 25 per cent was obtained. Under such conditions the length and thickness of the rubber strips diminished to one-half of their original dimensions.

When such a rubber band, 1 mm. wide and 0.3 mm. thick, was stressed by the gradual addition of small shot to a cup suspended at its lower end, rupture took place under a load of approximately 3 kilograms. When this breaking load was applied to the cross-section of the racked strip with the 250 per cent elongation, which in the preceding case was 0.3 sq. mm., the load at rupture was found to be 10 kg. per sq. mm. With still thinner strips, *viz.*, with cross-sections of 0.1 sq. mm., the loads at rupture were over 12 kilograms. These values approach the strength of viscose silk and of wool.[5]

Since in the present work, smoked sheet rubber after having been racked to 700–900 per cent gave tensile strengths of 0.8 to 1.5 kg. per sq. mm. (at 0° to 10° C.),[6] the difference between this and the approximately ten-fold higher strengths described above must be attributed to the colloid shellac-resin particles. The tremendous effect obtained by the addition of 20 per cent (by volume based on 100 volumes of rubber) is of the same order of magnitude as the maximum effect obtained from other active reënforcing agents.

Accompanying this great reënforcing effect of the colloid resin particles was a considerable diminution in extensibility and a stiffening (permanent elongation). Though pure Jatex films which had been stretched to the point of break in the stress-strain curve (450 to 500 per cent) showed a permanent elongation of 50 per cent of the original length, the films containing shellac resin showed 3 to 5 times this permanent elongation. This differing behavior of the two films is therefore analogous to that of mixtures containing colloidal silicic acid.[7]

With still higher loading, products were ultimately obtained which had properties resembling those of balata. By prolonged heating at elevated temperatures, *i. e.*, above 80° C., the toughening effect was to a great extent lost, probably because of coagulation and fusion of the shellac resin and the ammonium compounds of resin acids. Accordingly the toughening effect does not persist through vulcanization. Such thermally treated latex-shellac resin mixtures have properties similar to those of gutta-percha, and when hot are plastic and can be molded and extruded.[8]

In order to explain the phenomenona described above, resort must be had to experiments and ideas of earlier investigators on the same subject. Particular attention should be called to the fundamental work of Leblanc and Kröger,[9] which deals with the effects of compounding ingredients in unvulcanized rubber mixtures. Based on the work which Polanyi and Schob[10] carried out on the behavior of raw rubber at low temperatures, Leblanc and Kröger came to the conclusion that the marked increase in the tensile properties could be explained in the same way as could the effect of active reënforcing agents in rubber at ordinary temperatures. When distended rubber is chilled, the elongation is fixed, and the unstable condition which is capable of expending work is rendered stable, because the internal gliding planes are made stronger by the diminution in heat content, and because there is an increase in density. Accompanying this is a change in the tendency toward splitting, which is a decisive factor in the tensile strength. Polanyi and Schob found that considerable energy is required to rupture frozen rubber, and this can be the result only of an altered, *i. e.*, increased resistance to splitting at right angles to the direction of stretching as a result of the separation of microcrystalline rubber particles. As shown by Hock[11] in earlier experiments, the tendency (in the racked condition) to split in the direction of stretching remains on the contrary unaltered.

To explain the effect of compounding ingredients, the phenomena involved in rupture must be studied more thoroughly. Experiments have shown that rupture gives a smooth fracture, *i. e.*, a cleavage which is similar to the cleavage planes of crystals such as gypsum. These cleavage planes can be disrupted as can those of crystals, with accumulation of energy in the surrounding medium.

Such a disruption of the cleavage planes is effected by the presence of compounding ingredients, and in such a case considerable energy is absorbed upon stretching, and this energy is stored in the rubber and not in the pigment. As for rupture itself, it was found by Leblanc and Kröger to be characterized in two ways: (1) the greater the degree of dispersion of the pigment, the greater the number of disruptions of the cleavage plane and in turn the higher the tensile strength, and (2) the greater the energy of adsorption, the more extensive is the disruption. If there is no adsorption, there is no disruption of the cleavage planes.

These last conclusions are completely confirmed by results on the colloidal mixing of latex mixtures, as described by Norris.[12] This author calls attention to the necessity of the pigment having a particle size of approximately the same order of magnitude as that of the latex particles. Moreover his observation that, after drying and vulcanization, gas black has no reënforcing effect, is probably explainable by the fact that in such mixtures there is insufficient adsorption of the gas

black particles on the latex particles, in contrast to their behavior in dry latex rubber, where a reënforcing effect is obtained.

In the case of Jatex rubber-shellac mixtures, the conditions are different. Upon evaporation and drying, the ammonium resin soaps, which are colloidally dispersed (emulsified), deposit the resin chiefly on the surface of the undisturbed latex particles. These adsorbed enveloping films have a refractive index similar to that of rubber and therefore appear transparent. A certain amount of interglobular space is also filled with transparent amorphous glass-like resin.

It is clear that such a structure is isotropic in all directions, and therefore shows the same resistance to cutting in all directions. If a pull is exerted unilaterally on such a film, the latex particles become deformed and orient themselves parallel to the direction of the pull. At the same time the adsorbed enveloping films are ruptured at the locations where elongation occurs, and are partially coagulated by the increased internal friction. By a diminution in the adsorption and in the degree of dispersion of the resin phase, there occurs, in conformity with characterization (2) described above, a diminution in the extent of the disturbance in the direction of stretching of the cleavage planes, which represent the boundaries of the latex particles. This results in a greater tendency to rupture and less resistance to tearing in this direction.

Since this phenomenon is irreversible, the first effect persists even after the longitudinal deformation is removed by warming. The resistance to cutting at right angles to the direction of stretching diminishes slightly, probably because of a toughening of the rubber phase through deformation.

It is probable that the appearance of x-ray interferences in stretched and released films can be explained in a similar way. As a result of the stiffening effect of the coagulated and destroyed resin lamella, the latex particles (to an especially great extent the smallest particles) also persist in a deformed condition after release from tension. Whether because of the deformation of the latex particles, in the interior of which a lattice-like arrangement is created, or whether genuine crystals are formed, is a question by itself, and of no direct concern in the problem here.

If the phenomena are more complicated than assumed in the present discussion, it is in any case evident once more that, to explain the mechanical behavior of unmasticated raw rubber and its mixtures (latex mixtures), it must be assumed that the rubber particles as they exist in latex are the constructive elements of the whole system, and are also responsible for its essential physical properties. It is also evident from the foregoing discussion that the problem of the internal structure of these particles is of only secondary interest. One might easily imagine, in fact it must be assumed, that aggregates of colloidal particles are under certain conditions quite different in chemical composition from rubber, and yet closely resemble rubber in physical and particularly in mechanical properties.

Some Observations on the Resistance to Tearing of Vulcanized Rubber Sheets with a Calendar Grain

In view of the fact that the resistance of thin calendered rubber sheets to tearing, *e. g.*, football bladders, surgical goods, etc., is of just as much practical importance as is the resistance to cutting of products like tire treads and conveyor belt covers, some observations pertinent to this subject may well be discussed.

It is well known that the extensibility and tensile strength of most calendered sheets are different in the direction of calendering from the values in a direction at right angles to this, and from this has come the idea of calender or mill grain. In turn it is necessary to distinguish between the true calender grain (calender effect) which results from deformation of the latex particles which are still to some

extent present in the masticated rubber, and the mill grain (grain effect) which is brought about especially by the addition of powders with a pronounced directional shape, *e. g.*, mica and basic magnesium carbonate, because of their parallel orientation.

Though the true calender effect can to a large extent be destroyed by thermal treatment of the sheets before vulcanization, the mill grain (grain effect) persists after vulcanization, because of the rigidity of the oriented particles. As a result, such rubber sheets show anisotropic mechanical properties.[13]

Thus the tensile strength of such anisotropic sheets is frequently 10 to 20 per cent higher in the direction of calendering, while the extensibility in the same direction is correspondingly less. This phenomenon is not always so distinct in the values of the elongation at rupture, because with the lower tensile strength at right angles to the direction of stretching, rupture usually takes place at an actually lower elongation than it does in the direction of milling. These phenomena

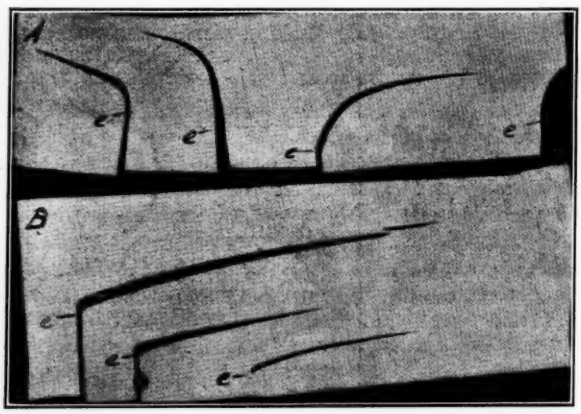

Figure 2—Tearing Curves of Calendered Vulcanized Rubber Sheets

A. Active filler *B*. Inactive filler
The marks *e* represents the points to which razor cuts were carried.

have recently been described by Jones,[14] and previous to this Somerville[15] showed the influence of the calender grain on the stress-strain curves of samples which had been cut in the direction of calendering and at right angles to this direction.

Besides these differences in tensile strength and extensibility, calendered sheets frequently show differences in resistance to cutting and to tearing in the two directions. As is known, the direction of calendering of a sheet can be established in this way, while upon further tearing after cutting in a particular direction, the tear continues in the direction of the least resistance, which is the direction of calendering.[16] The form of the tearing curve is quite characteristic of a given vulcanizate and of vulcanizates of the same quality, and may be considered as a const. of the material.

In Fig. 2 the tearing curves of two different rubber bed sheetings are shown, the torn sheets being copied directly on carbon paper.

The form of the tearing curves is naturally dependent upon the relation between the resistance to tear and the magnitude of the grain effect. In Fig. 2 the upper curves pertain to rubber (Quality A) with a relatively high resistance to cutting and

a slight grain effect, while the lower curves represent a rubber of B quality with the opposite behavior. Here at the points where the cuts stop, the tears immediately take the direction of the milling.

In Table II, which follows, the tensile strengths, elongations at rupture, and resistances to tearing of the samples of Quality A and Quality B are given. Quality A contained 45 per cent of an active reënforcing agent (amorphous silicic acid), whereas Quality B contained an inactive filler.

TABLE II

TENSILE STRENGTHS, ELONGATIONS AT RUPTURE, AND RESISTANCES TO TEARING OF BED SHEET RUBBER, 0.5 MM. THICK, 15 MM. WIDE AND 80 MM. LONG

	Tensile Strength (Kg. per Sq. Cm.)		Elongation (Per Cent)		
Quality	Calender Direction	Right Angles to Calender Direction	Calender Direction	Right Angles to Calender Direction	Tear-Resistance (Grams per Mm. Thickness)
A	86	76	295	300	280
B	46	36	220	215	70

The resistances to tearing frequently change both during natural and artificial aging to a different extent than do the tensile strengths, and the greater the calender grain the greater are these changes.

Table III gives the tests obtained on the same samples shown in Table II, but after 72 hours of heating in an oven at 70° C.

TABLE III

TENSILE STRENGTHS, ELONGATIONS AT RUPTURE, AND RESISTANCES TO TEARING OF THE SAMPLES IN TABLE II, AFTER 72 HOURS OF AGING IN AN OVEN AT 70° C.

	Tensile Strength (Kg. per Sq. Cm.)		Elongation (Per Cent)		
Quality	Calender Direction	Right Angles to Calender Direction	Calender Direction	Right Angles to Calender Direction	Tear-Resistance (Grams per Mm. Thickness)
A	58.5	54.5	230	260	200
Decrease (per cent)	33	29.5	22	13	25
B	34.6	31.0	125	120	42
Decrease (per cent)	24.8	14	43	44	40

Though in the case of the samples of A quality, the diminution in resistance to tearing in a direction at right angles to the direction of calendering was of the same order of magnitude as the reduction in tensile strength, in the case of the sample of B quality the reduction was almost three times as much.

The tabulated results show further the influence of the nature of the filler on the resistance to tearing. The sample of A quality with an active filler had a resistance to tearing four times as great as that of the sample of quality B containing an inactive filler.

These differences are still more evident in the samples which had been aged in the oven. It is also seen that the diminution in the resistance to tearing was in neither case of the same order of magnitude as that of the loss in tensile strength in either direction, a phenomenon which in practice may have disagreeable consequences. This phenomenon appears to be analogous to the observation of de Visser that sheets with a calender grain deteriorate to a greater extent in the direction of calendering than in a direction at right angles to this.

Measurement of the Tensile Strength and Resistance to Tearing of Calendered Rubber Sheets

In conclusion, some points regarding measurements of the tensile strengths and resistances to tearing of thin calendered sheets of rubber may be mentioned. The ordinary Schopper tensile machine is not suitable for measurements such as these, because the actual strengths are so small that the machine is not precise in the particular range. On the other hand the Schopper yarn tester of the same manufacturer, *viz.*, Model No. 1510, gives very satisfactory results.

For the tensile strength measurements, strips 15 mm. wide and 100 mm. long are used, and these are cut and torn in a direction at right angles to the calendering direction. Their ends are placed in folded strips of felt in the clamps of the machine.

The same kind of strips are used for measuring the resistance to tearing, in which case the strips are first cut with a razor blade for several centimeters in the direction of calendering. In measuring the resistance to tearing, the weight of the lever arm is deducted. The same rate of separation is used throughout, *viz.*, approximately 1 centimeter per second, since this rate has a considerable influence on the results.

In case there is no scale for loads without the lever weight, the scale at hand is calibrated by suspending a corresponding weight on the upper clamp. Very small tearing stresses can be measured with this machine, in fact the results obtainable are sufficiently precise for practical purposes.

References

[1] *Kautschuk*, **9**, 82, 100 (1933).

[2] Jatex is prepared by centrifuging *Hevea* latex until a concentrated latex containing 60 per cent of rubber is obtained.

[3] *Kolloidchem. Beihefte*, **21**, 193 (1925).

[4] The x-ray diagrams were made by G. von Susich in the laboratories of the I. G. Farbenindustrie A.-G., Ludwigshafen a. Rh.

[5] Karger and Schmidt, *Z. angew. Chem.*, **39**, 299 (1926).

[6] *Kautschuk*, **2**, 151 (1925).

[7] Kirchhof, *Gummi-Ztg.*, **39**, 2012 (1925).

[8] Powdered latex mixtures and artificial gutta-percha (Gutta-Alco) are essentially the same type of mixtures. See *Kautschuk*, **9**, 47 (1933).

[9] *Z. Elektrochem.*, **34**, 725 (1928); *Kolloid-Z.*, **45**, 16 (1928); de Visser, "Kalanderund Schrumpfeffekt von unvulkanisiertem Kautschuk," *Dissertation* Delft, **1925**.

[10] *Mitt. d. Mpa*, **42**, 22 (1924).

[11] *Z. Elektrochem.*, **31**, 407 (1925); *Gummi-Ztg.*, **39**, 1746 (1925); *Kautschuk*, **1**, Oct., 1925.

[12] *India Rubber World*, **86**, 35 (1932). Hock ("Handbuch d. Kautschuk-Wissenschaft," page 563) has pointed out the increasing importance of a study of this phase of the mixing art.

[13] Wiegand and Braendle, *Ind. Eng. Chem.*, **15**, 259 (1923). In regard to the other comprehensive literature on calendering and mill grain, see in the *Handbuch der Kautschukwissenschaft*, an article entitled "Physik des Kautschuks."

[14] *Trans. Inst. Rubber Ind.*, **7**, 48 (1931); RUBBER CHEM. & TECH., **5**, 351 (1932).

[15] *Kautschuk*, **6**, 172 (1930).

[16] When homogeneous sheets are torn in the direction of milling, the tear naturally does not turn and continue at right angles to this direction, since the resistance to tearing is greater in this direction.

[Reprinted from Transactions of the Institution of the Rubber Industry, Vol. 9, No. 3, pages 190–195, October, 1933.]

Solution Properties of Dried Rubber

T. H. Messenger

References to the properties of raw rubber dried to a point beyond that of ordinary commercial practice are very scanty. The Rubber Research Scheme is at present engaged in a comprehensive investigation into the factors governing the plasticity of raw rubber, and has found that humidity conditions during storage may greatly affect this property. Thus, storage in a dry atmosphere (over calcium chloride) leads to greater hardness (Ceylon Rubber Research Scheme, *2nd Quarterly Circ.*, **1929,** p. 1), and storage in dry nitrogen (and it is presumed, in any dry inert medium) has a similar effect (Martin and Elliott, Ceylon Rubber Research Scheme, *Quarterly Circ.*, **8,** 7 (1931)). Staudinger and Bondy have used vacuum drying in their work on fractionating raw rubber (*Ann.*, **488,** 153 (1931)).

Some years ago the writer had occasion to dry a small sample of rubber by passing over it at about 60° C. a stream of hydrogen dried by contact with phosphorus pentoxide. It was observed that after drying the rubber was very difficult to bring into solution in benzene. This suggested the experiments described in the present note, which were initiated to examine the effect of thorough drying on the solution properties of raw rubber.

Experimental.—The method adopted was to masticate pale crepe for various periods, and store a range of samples of each milling at a reduced pressure over phosphorus pentoxide. From time to time samples were withdrawn, and the viscosity of a benzene solution was measured. In some cases the amount of rubber passing into solution was determined also. A subsequent experiment consisted in preparing the solution from the undried rubber and observing the viscosity as the solution itself was dried over phosphorus pentoxide.

Four degrees of milling were employed: A, unmilled; B, lightly milled; C, normally milled; D, overmilled pale crepe rubber. Milling was conducted on cold rolls, and the rubber was then allowed to rest for 60–61 days at a uniform temperature of 25° C. Previous work had indicated that this rest period was adequate to permit the milled rubber to recover to a comparatively steady state. At the conclusion of the rest period samples from each milling were accurately weighed out so that on dissolving in 50 cc. benzene at 25° C. the solutions would have the following concentrations, expressed as per cent by weight: A, 1 per cent; B, 2 per cent; C and D, 3 per cent.

Each weighed sample was then placed in one limb of a separate drying tube (for description and illustration see Messenger, *Trans. Inst. Rubber Ind.*, **5,** 71 (1929)), phosphorus pentoxide was introduced into the other limb, and the tube was evacuated at the water pump and sealed. The tubes were then stored at 25° C. in the dark until required. (Occasional deviations from 25° C. occurred, owing to a defective thermostat.) The desired drying period having elapsed, the tubes were opened, the rubber was cut into small pieces and dissolved in pure benzene (A. R. quality) to give the above-mentioned concentrations. No attempt was made to use specially dried benzene. After standing overnight the solutions were shaken in a mechanical shaker for $6^1/_2$ hours, though in cases when the rubber dissolved easily a shorter shaking was practicable and given. Light was excluded as much as possible during these operations. The viscosities of the resulting solutions were determined at 25° C., the results being expressed in centipoises.

As drying proceeded it was found that in the cases of the unmilled and lightly milled rubbers, some of the material refused to dissolve, even on prolonged shaking. This was filtered off by means of coarse muslin before determining the viscosity, and the rubber content of the liquid was measured. It should be noted that

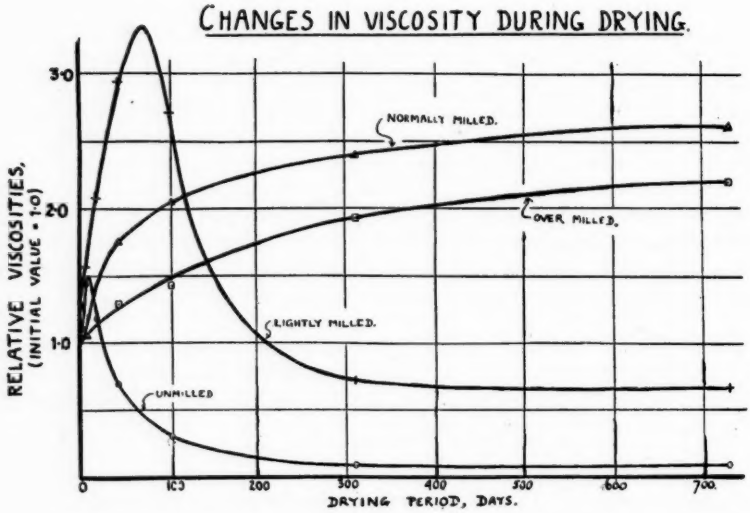

Figure 1

before drying, all the rubbers were completely soluble, and gave perfectly homogeneous solutions.

The following results were obtained and are set out in graphical (Fig. 1) and tabular form. Observed viscosities are tabulated together with relative viscosities, the initial value of each series being referred to as unity. It is the relative figures that appear in the curves.

	A, Unmilled			B, Lightly Milled		
	Viscosity			Viscosity		
Days	Centi-poises	Relative	%, Insoluble	Centi-poises	Relative	%, Insoluble
0	28.9	1.00	0.0	54.4	1.00	0.0
2	31.4	1.09	0.0	69.8	1.28	0.0
6	41.5	1.44	0.6	85.6	1.58	0.0
16	34.2	1.18	3.5	112.8	2.08	0.0
41	19.5	0.68	13.5	159.3	2.93	0.0
98	8.66	0.30	34.2	146.1	2.70	0.0
308	2.55	0.09	53.0	37.1	0.70	10.5
734	3.01	0.10	54.7	35.8	0.66	14.0
	Control, Undried			Control, Undried		
6	28.9	1.00	0.0	54.4	1.00	0.0
114	25.0	0.86	0.0	68.4	1.26	0.0
335	26.4	0.91	0.0	70.6	1.28	0.0
741	24.0	0.83	0.0	61.9	1.12	0.0

	C, Normally Milled			D, Overmilled		
0	21.4	1.00	0.0	5.01	1.00	0.0
2	22.2	1.04	0.0	...	...	..
6	22.4	1.05	0.0	5.32	1.06	0.0
41	37.1	1.74	0.0	6.45	1.29	0.0
98	43.7	2.04	0.0	7.11	1.42	0.0
308	50.1	2.34	15.0	9.64	1.92	0.0
734	55.1	2.58	2.0	10.8	2.16	0.0
	Control, Undried			Control, Undried		
8	21.4	1.00	0.0	5.01	1.00	0.0
114	21.3	1.00	0.0	5.19	1.04	0.0
741	30.5	1.43	0.0	5.71	1.19	0.0

It will be noticed that the following changes accompany drying: (1) a very marked increase in the solution viscosity (over 3 times the original in the case of rubber B), followed in rubbers A and B by a less rapid decrease to a value much below the original; (2) in the case of rubber A a portion of the rubber becomes insoluble in benzene under the conditions of the experiment, the proportion of insoluble component increasing progressively with time of drying, though the rate of this progress falls off continuously. The phenomenon is apparent to a lesser degree in rubbers B and C.

Both changes progress more slowly as milling increases in severity. Thus, in rubber A (no milling) the maximum viscosity is reached in 5 or 6 days, in rubber B (light milling) in 70 days, whereas in the other two rubbers it is not certain that the maximum has been attained after more than 700 days.

There can be no doubt that some real change has been brought about by intensive drying, since though viscosity changes occur in the controls, which were stored with the experimental samples but not dried, they are irregular and much smaller. Moreover, the pronounced fall in viscosity in the later stages, owing to a portion of the rubber having become insoluble, giving a less concentrated solution, is not observed in rubbers as normally stored. This is confirmed by the curious change in solubility, most evident in rubber A. So marked was this feature that the solutions of this rubber, dried for periods of 16 days and upwards, which were very thin and mobile, could easily be decanted from the swollen but insoluble lumps. If the whole mixture was allowed to stand for a week with intermittent shaking these lumps were broken up into smaller particles, but the resulting liquid was very heterogeneous, containing lumps. The addition of water to the mixture did not render the insoluble portion soluble again.

Milling weakens the rubber and causes it to be more sensitive to shaking, so that the insolubility is less apparent in rubbers B and C, as revealed by measurements of the rubber contents of the filtered solutions. However, the phenomenon is present, and the solutions of these rubbers after 41 days for rubber B and 308 days for C were granular, but the lumps were so soft that filtering was extremely difficult. Rubber D gave smooth solutions over the whole period.

It is worthy of remark that although nearly 50 per cent of rubber A was still soluble after 734 days' drying, yet the viscosity had fallen to a value only one-tenth the original. Part of this fall in viscosity is due to the more dilute solution formed by the dried rubber, but the determination of the viscosity of a solution of undried rubber equal in concentration to that from the dried rubber has shown that concentration alone is not a sufficient explanation of the change. The figures are as follows:

Rubber	Cp.
1% solution, 0 days' drying	28.9
0.453% solution, 734 days' drying	3.01
0.453% solution, 0 days' drying	4.97

These results suggest that drying has had a definite effect on the rubber, for example, by preferentially converting an initially more viscous fraction into the insoluble form observed. The two fractions, more or less viscous, suggested by

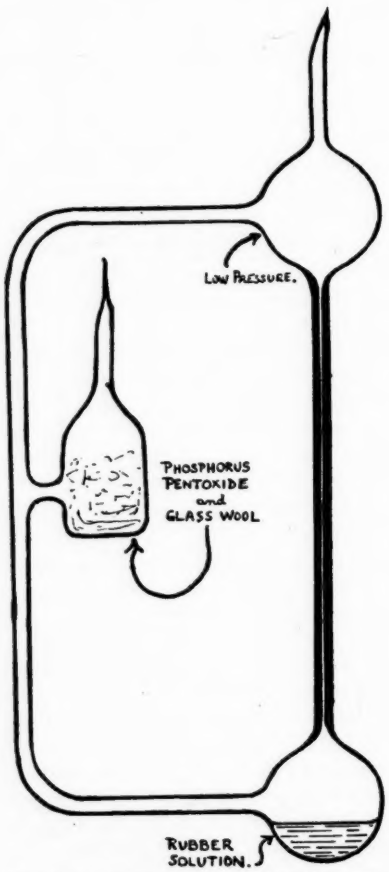

Figure 2—Apparatus for Observing Viscosity of Rubber Solution during Drying

this hypothesis may be identical with or related to the gel- and sol-rubbers described by Pummerer and Miedel, who found that the gel fraction (insoluble in ether) might constitute 45 per cent of the total rubber (*Ber.*, **60**, 2148 (1927)).

Experiments with Solutions.—The foregoing experiments were supplemented by investigations into the behavior as regards viscosity of rubber solutions during drying, this work being concerned with the drying of the solution itself as distinct from only the rubber being dried.

For this purpose two solvents were chosen, benzene and carbon tetrachloride. Both were A. R. quality, the former being further treated with concentrated sulfuric acid and redistilled to remove any traces of thiophene, and the latter saturated with chlorine, boiled to expel chlorine, allowed to stand over solid potassium hydroxide and redistilled. Rubber B (lightly milled) was chosen; a 1 per cent solution in benzene and a 0.7 per cent solution in carbon tetrachloride were prepared, both percentages being expressed by weight.

About 15–20 cc. of solution were then introduced into the specially designed drying apparatus shown in Fig. 2, after which the pressure was reduced till the solvent commenced to boil, and the tube immediately sealed. The drying agent was phosphorus pentoxide distributed over glass wool. The apparatus was designed to permit viscosity readings without opening the tube, the apparatus being inverted and the time required for the whole of the liquid to flow through the capillary being observed. This measurement was always made at 25° C. in dim light. The tubes were stored in a warm room and in darkness. The solution never came into contact with the desiccating agent, drying being effected by the removal of water vapor.

Contrary to expectation no rise in viscosity accompanied drying. No significant changes occurred in the benzene solution, while that in carbon tetrachloride showed a continuous decrease in viscosity. It is possible that this was due to the development of slight acidity in the solvent during the period of the experiment, leading to electro-viscous changes in the rubber, as described by de Vries (*India Rubber J.*, **67,** 849 (1924); *Archief*, **9,** 294 (1925)).

Readings were as follows:

Benzene Solution		Carbon Tetrachloride Solution	
Days Dried	Viscosity Cp.	Days Dried	Viscosity Cp.
0	9.35	0	36.8
13	9.61	28	35.3
41	9.50	139	31.4
152	9.79	274	21.9
287	9.20		

Conclusions.—No simple explanation of the foregoing changes suggests itself. It would appear that intensive drying leads to some kind of aggregation, association, or polymerization in the rubber molecule, even in the case of rubber which has not been subjected to any milling beyond what little it may have suffered on the plantation. This is evidenced by the rise in viscosity and by the development of an insoluble component. Such molecular association is not unknown, and has been held responsible for the surprising changes in boiling point and other properties of the pure liquids subjected to intensive drying by Baker (*J. Chem. Soc.*, **1922,** 568).

The author is indebted to the Board of Management of the Research Association of British Rubber Manufacturers for facilities for carrying out the work.

[Translated for Rubber Chemistry and Technology from the Kolloid Zeitschrift, Vol. 65, No. 3, 350–355, December, 1933.]

Investigation of the Aging Processes in Rubber

I. The Effect of Irradiation with Ultra-violet Light on the Surface Tension of Rubber Solutions

B. Dogadkin and G. Pantschenkow

Institute of the Rubber Industry, Moscow

In one of our previous publications,[1] we showed that the surface tension at the boundary: benzene solution/water, of a rubber solution diminishes greatly when the solution is irradiated with a quartz lamp. This diminution is doubtless related in some way to the formation of oxidation products of the rubber. Such products naturally possess a high surface activity, since they are composed of ruptured sections of molecular chains on which polar groups rich in oxygen (CHO, CO_2H, and CH_2OH) are arranged asymmetrically.

According to the Traube law, the longer the hydrocarbon or the higher the molecular weight, the greater is the surface activity of the oxidation products. Consequently the change in the surface tension must be particularly great in the first stage of the oxidation of the rubber, *i. e.*, at the very time when ordinary analytical methods are incapable of detecting the presence of oxidation products.

In view of all this, it appeared very much worth while to have recourse to surface tension methods for studying problems connected with the aging of rubber, especially for investigating the changes in rubber which take place under the influence of ultra-violet radiation.

In spite of numerous investigations dealing with the effect of light on rubber, the phenomena involved are still far from being explained. In the opinion of Henri,[2] rubber when exposed to ultra-violet radiation undergoes an accelerated oxidation, while in the opinion of van Rossem[3] light exerts an independent action on rubber in that it causes depolymerization. Asano,[4] who studied this problem in a particularly thorough manner, offers the opinion that light causes either polymerization or depolymerization of rubber, according to the wave length. However his conclusions cannot be regarded as having settled the problem, because of the extraordinary difficulties in carrying out experiments in the absence of oxygen. Dufraisse[5] lays particular emphasis on this point, and regards the deterioration of rubber as a catalytic oxidation process. As a result of the interesting investigations of Cotton[6] and Busse,[7] who showed that the changes in properties which rubber undergoes during mastication (plasticizing) are the result of changes brought about by oxygen, there is a growing number of adherents of the idea that the changes in rubber induced by ultra-violet light can be explained in a similar manner.

Nevertheless, in our opinion the well-established investigations on the oxidation process during aging do not exclude the possibility of an independent action of light on rubber, particularly since such an action is necessary to explain the condition of the colloidal and chemical nature of the rubber.

I. Experimental Part

To prove that light may act directly upon rubber, benzene solutions of rubber were irradiated with a quartz lamp, both in air and in an inert gas. The changes in

the condition of the rubber were followed by measuring the viscosity and the surface tension at the boundary with water. The surface tension values also served to judge the intensity of the oxidation. The experiments were first of all carried out with rubber which was prepared from pale crepe by a method already described in a previous publication.[8]

It was found, however, that this particular method of purification did not fulfil the necessary conditions because of the use of carbon dioxide as the inert gas. Accordingly a special apparatus, illustrated in Fig. 1, was devised for purifying and irradiating the rubber.

This apparatus consists of three receptacles connected with one another by a system of tubes with stopcocks designed to insulate the lubricant from the liquids. Receptacles B and C are connected to burettes which are graduated to 0.1 cc. The burettes are connected in turn with a quartz flask D, which is provided with a

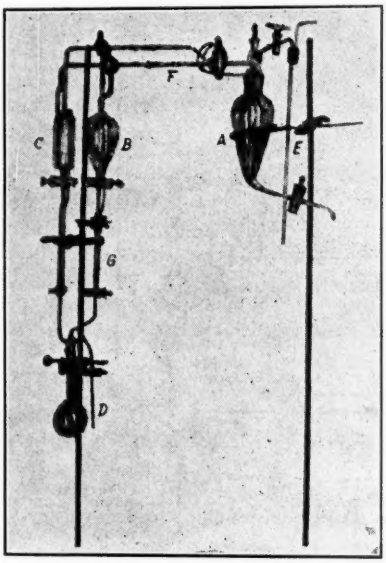

Figure 1

syphon for removing the samples. Receptacle A is connected by means of tube E with a tall cylinder (not shown in Fig. 1), and through this with a supply of nitrogen (free of oxygen). The nitrogen is led from its steel tank through a series of absorption vessels and then through a copper screen heated in an electric oven at 600–700° C., in order to purify it from oxygen and from traces of sulfur dioxide. It is then led through an apparatus which absorbs traces of oxygen. In this latter apparatus the gas passes through a coil filled with aqueous sodium plumbite, is then sprayed through a Schott filter, thence through a layer (0.5 meter deep) of an alkaline solution of sodium hydrosulfite, and finally through a system of drying coils and columns. As is known, this method of purification assures a complete removal of oxygen from the nitrogen.

All preliminary operations in the purification of the rubber, including washing with ammonia solution, preparation of the solutions, emulsification, and precipita-

tion with acetone, were carried out in closed receptacles filled with nitrogen. The liquids were likewise saturated with nitrogen. The extraction with acetone was carried out in a Rodermacher apparatus, to the flask of which was attached a tube for leading in nitrogen in a continuous current. The adapter of the condenser was closed by a rubber valve.

The extracted rubber was transferred immediately to receptacle A, which had been previously evacuated and completely filled with nitrogen (the nitrogen was passed through the whole system for two hours). Before thus passing the nitrogen through, receptacles C and A were filled with freshly distilled benzene which had been saturated cryoscopically with nitrogen. The dissolved rubber was fractionally precipitated by acetone by the method of Pummerer and Miedel.[9] The acetone was driven out of cylinder E by the pressure of nitrogen.

The heavy fraction of the rubber was precipitated in the narrow part of receptacle A, and then removed, with part of the solution, through the lower large stopcock. In this way the mother liquor was removed after sedimentation of the rubber.

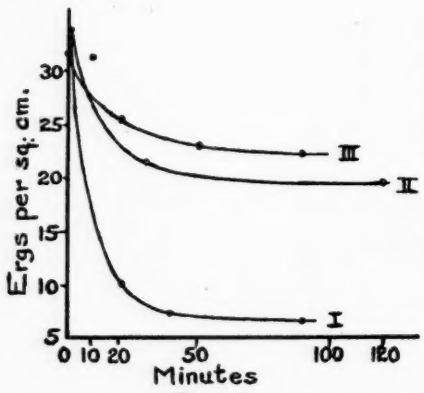

Figure 2

I. 1.5 per cent solution irradiated in air.
II. 1.5 per cent solution irradiated in carbon dioxide.
III. 0.5 per cent solution irradiated in carbon dioxide.

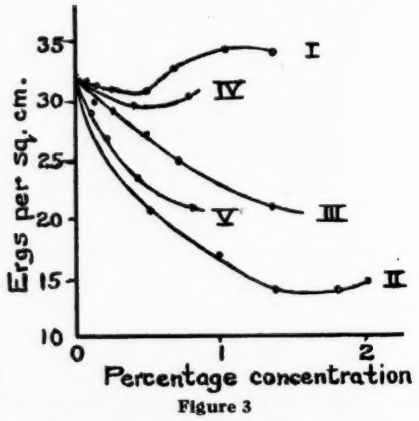

Figure 3

I. Sample K_1 before irradiation.
II. Sample K_1 after irradiation in air.
III. Sample K_1 after irradiation in carbon dioxide.
IV. Sample K_2 before and after irradiation in nitrogen.
V. Sample K_2 after irradiation in air.

The precipitated light fraction was freed of acetone by a current of nitrogen through the receptacle for several hours. The precipitate was then washed by means of a rapid current of benzene from cylinder E, and was again dissolved in benzene saturated with nitrogen. The solution was forced through tube F into receptacle B, and was kept in the latter, protected from light by tinfoil. The quantity of solution necessary for the experiments was measured by burette G, and was then introduced into the quartz flask D, where it was exposed to the effects of the quartz lamp.

After irradiation, the solution was forced through a syphon into a small receptacle, containing water and filled with nitrogen, in order to measure the surface tension. This latter measurement was carried out according to the procedure described in the previous work.

The results of the measurements are summarized in Tables I and II, and are also shown graphically in Figs. 2 and 3.

Preparation K_1, in Table II, signifies rubber which had been purified according to the method described in the earlier work, while K_2 and K_3 signify samples which were purified and irradiated by the apparatus described in the present work.

It is obvious from Table I that the change in surface tension during the first thirty minutes of irradiation was particularly great. The kinetics of this phenomenon are similar to those of the change in viscosity which takes place under the influence of the same radiation. The process was considered to be complete after 120 minutes, and this period of time was maintained in determining the values given in Table II.

TABLE I

THE CHANGE OF THE SURFACE TENSION WITH IRRADIATION. RUBBER PREPARATION K_1

$$\sigma \frac{\text{Water}}{\text{Benzene}} = 32.3 \frac{\text{Erg}}{\text{Sq. Cm.}}$$

Time Irradiated (Minutes)	Surface Tension in Ergs per Sq. Cm. for Solutions of 1.5% Irradiated in Air	1.5% Irradiated in CO_2	0.5% Irradiated in CO_2
0	33.21	33.21	31.37
10	...	...	31.05
20	9.85	...	24.94
30	...	21.03	...
40	7.04	...	...
50	...	...	22.88
90	6.64	...	21.96
120	...	19.47	...

TABLE II

SURFACE TENSION AT THE BOUNDARY: WATER-RUBBER SOLUTION, BEFORE AND AFTER IRRADIATION FOR 120 MINUTES

Concentration in Per Cent	Preparation K_1: Before Irradiation	Preparation K_1: After Irradiation in Air	Preparation K_1: After Irradiation in CO_2	Preparation K_2: Before Irradiation	Preparation K_2: After Irradiation in Air	Preparation K_2: After Irradiation in Nitrogen	Preparation K_3: Before Irradiation	Preparation K_3: After Irradiation in Nitrogen
0.	32.30	32.30	32.30	32.30	32.30	32.30	32.30	32.30
0.101	...	...	...	31.82	28.65	31.82	...	...
0.125	31.87	25.20	29.91	...	...	...	...	...
0.170	...	...	...	...	...	...	32.43	31.83
0.203	...	...	...	31.46	26.94	31.70	...	...
0.250	30.96	21.08	29.55	...	...	...	...	...
0.340	...	...	...	...	...	...	31.46	31.60
0.405	...	...	...	29.83	23.38	29.83	...	...
0.500	30.83	20.87	27.46	...	...	...	...	...
0.680	...	...	...	...	...	...	30.31	30.01
0.700	33.10	19.35	24.76	...	...	...	...	...
0.810	...	...	...	31.83	20.55	31.81	...	...
1.000	34.16	16.90	23.39	...	...	...	...	...
1.360	34.19	13.96	21.00	...	...	...	32.96	29.75
1.500	...	...	...	...	...	...	...	...
2.000	...	16.90	...	...	...	...	...	...

As already mentioned, the changes in the state of the rubber were also followed by observing the changes in the viscosity of its solutions. The results are shown in Table III.

II. Discussion of the Results

The values given in Table II verify the character of the surface tension isotherms of rubbers already discussed in the previous work. The minimum of the isotherm occurs in the concentration range of 0.4 to 0.7 per cent. Irradiation in the presence

TABLE III

THE VISCOSITY OF RUBBER SOLUTIONS BEFORE AND AFTER IRRADIATION
Ostwald's Viscometer; $r = 0.038$; $t = 20°$ C.

	Preparation K_2			Preparation K_2	
Concentration in Per Cent	$\frac{Tk}{Tl}$ before Irradiation	$\frac{Tk}{Tl}$ after Irradiation in Air	$\frac{Tk}{Tl}$ after Irradiation in Nitrogen	$\frac{Tk}{Tl}$ before Irradiation	$\frac{Tk}{Tl}$ after Irradiation in Nitrogen
0.101	1.80	1.29	1.60	...	...
0.203	3.40	1.69	3.10	...	...
0.315	...	..	...	3.60	2.88
0.405	10.50	2.81	8.30	...	...
0.630	...	..	...	13.78	6.67
0.810	46.20	5.87	27.50	...	...
1.260	...	..	...	77.23	24.00

of oxygen changed the character of the isotherm rather sharply. In all the concentrations which were measured, the surface tension at the boundary: benzene/water, was considerably lower than that of a solution which had not been irradiated. As already mentioned, this lowering of the surface tension indicates the formation of surface-active, oxygenated decomposition products of the rubber. There is no doubt that these products contain substances which have acid properties in water. This is indicated by the work of Gorter,[10] as well as by that of Kemp, Bishop, and Laselle.[11]

This was proved in the following manner. The rubber solution was agitated with water, both before and after irradiation, after which the electrical conductivities of the water extracts were determined. The results of these determinations are summarized in Table IV.

TABLE IV

Sample Tested	Specific Electric Conductivity, K
Water	0.656×10^{-5}
Extract from pure benzene	0.612×10^{-5}
Extract from 2 per cent rubber solution before irradiation	0.657×10^{-5}
Extract after irradiation in air	0.924×10^{-4}

Irradiation in air led to the formation of substances, the electrical conductivities of which were considerable.

Judged by the literature,[12] it was at first thought that the increase in electrical conductivity was chiefly the result of the presence of levulinic acid. This supposition was not however tenable in view of the electrical conductivity of aqueous solutions of levulinic acid, and the effect of the latter on the surface tension at the boundary: benzene/water. The characteristic behavior of levulinic acid in this respect is shown in Table V, below, which gives the measurements obtained.

TABLE V

Concentration of Levulinic Acid (in Per Cent)	Specific Conductivity (K)	σ of the Boundary with Benzene (in Ergs per Sq. Cm.)
0.08	0.172×10^{-3}	...
0.16	0.240×10^{-3}	31.57
0.50	.....	30.65
0.72	0.460×10^{-3}	28.19
1.43	0.627×10^{-3}	25.20
2.00	.....	26.60
2.82	0.838×10^{-3}	...

These results compel one to assume that by irradiation in the presence of air, the oxidation processes which ensue lead to the formation of acids with a far greater number of carbon atoms than levulinic acid contains. It is of course possible that there is a certain amount of levulinic acid among these products.

As is evident from Table II, oxidation also took place during irradiation of preparation K_1 in an atmosphere of carbon dioxide. In this case there was a distinct lowering of the surface tension, though the lowering was less pronounced than that caused by irradiation in the presence of air. Oxidation appears to have taken place, judged by calculations of the oxygen absorbed during transfer of the rubber solution into the quartz flask. In this experiment irradiation was carried out with the flask not connected directly with the receptacle containing the solution.

There was probably also decomposition of carbon dioxide into oxygen and carbon monoxide, from the effect of short wave lengths. Attention has been called to this phenomenon by Bruni and Pelizolla[13] in their discussion of the work of Asano and of van Rossem. In any case this shows the difficulties in carrying out experiments in the absence of oxygen, and the necessity of using nitrogen as the inert gas.

In the irradiation of the rubber solutions (samples K_2 and K_3) in an atmosphere of nitrogen, where all the precautionary measures described were carried out, it is the opinion of the authors that the conditions were such that the rubber was really exposed to ultra-violet radiation in the absence of oxygen and of substances containing oxygen. This is indicated by the fact that the surface tension remained unaltered throughout the irradiation. At the same time, the considerable lowering of the viscosity of the solutions (see Table III) was unquestionably the result of structural changes in the rubber. The authors are therefore inclined to believe that the experiments described in the present paper confirm the view of Asano, Kirchhof, and van Rossem, that there is possibly another independent effect of oxygen, even in its absence, on the rubber. In the experiments of Asano, this influence leads either to polymerization or to depolymerization of the rubber, depending upon the wave length.

In the present experiments, the changes in viscosity indicate that the effect is a depolymerization of the molecules or a disaggregation of the micelles. Based on the general concepts of photochemical processes, it is necessary first of all to consider the influence of the radiant energy on the individual molecules, which in solutions of certain concentrations coexist, in the opinion of the present authors,[14] with micelles or aggregates of rubber.

The light quanta apparently bring about decomposition of the molecules, according to a reaction represented in simple form as follows:

$$(C_5H_8)_n + h_\nu = (C_5H_8)_{n-m} + (C_5H_8)_m.$$

Considering the structural peculiarities of rubber molecules, *e. g.*, the great number of degrees of freedom, it is probable that photochemical dissociation takes place at the temperatures in question. It may also be assumed that photochemical dissociation takes place not only in the case of free rubber molecules, but also in the case of molecules which exist in the micellar or aggregated state. Supposing this to be so, then the dissociation or even the simple excitation of a certain number of molecules might lead to dissociation (disaggregation) of the micelles themselves. The liberation of the intramicellar fluid would lead in turn to a lowering of the viscosity of the solutions. This was actually found to be true experimentally.

It should be mentioned further that the reduction in the viscosity after irradiation was relatively great in concentrated solutions, which indicates that the secondary process, *viz.*, dissociation of the micelles, outweighs the dissociation of the indi-

vidual rubber molecules. The constancy of the surface tension during irradiation in an atmosphere of nitrogen, in contrast to changes in the viscosity, conforms perfectly with the earlier opinion of the authors[15] regarding the causes of the surface activity of rubber. The polarity of rubber is determined by the polarity of the isoprene nucleus, and it does not change in any significant way with a change in the number of the nuclei in the rubber molecule. This explains why the depolymerization process, which is initiated by the action of light in the absence of oxygen, does not lower the minimum of the isotherm of the surface tension.

In conclusion there is one more phenomenon to be considered. The diminution in the viscosity of rubber solutions is not so great when irradiation is carried in an inert gas as it is in the presence of air. Such a phenomenon can be explained by the fact that rubber solutions contain molecules of widely different dimensions, *i. e.*, of differing degrees of polymerization, and which differ in a corresponding way in their light absorption.

We hope to carry out in the near future a qualitative and quantitative investigation by spectrometric methods of the photochemical dissociation of rubber.

Summary

1. Irradiation of rubber solutions in the presence of air with ultra-violet light brings about a pronounced lowering of their surface tensions at the boundary of solution and water. This lowering is connected with the formation of oxidation products of rubber, which are surface-active.

2. The kinetics of the changes in the surface tension are similar to those of the changes in viscosity brought about by irradiation of the solutions.

3. Irradiation of solutions of purified rubber in an atmosphere of nitrogen does not bring about any change in their surface tensions, as judged by the values of the minima of their isotherms.

4. These facts show that, in the absence of oxygen, light may exert an independent effect on rubber by causing depolarization of the rubber molecules and disaggregation of the micelles, which is closely related to this depolarization. In a general way, the nature of the action of light on rubber and the conditions necessary for the light to be effective are explained by the present work.

In conclusion, the authors wish to express their appreciation to Professor A. A. Seide for his kindness in furnishing the samples necessary for the work.

References

[1] Dogadkin and Pantschenkow, *Kautschuk*, **7**, 198, 217 (1931); *Z. anorg. allgem. Chem.* (Russ.), **1** (63), 994 (1931); RUBBER CHEM. & TECH., **5**, 249 (1932).

[2] Henri, *Caoutchouc et gutta-percha*, **7**, 4371 (1910).

[3] van Rossem, *India Rubber J.*, **48**, 172 (1914); *Kolloidchem. Beihefte*, **10**, 28 (1918).

[4] Asano, *India Rubber J.*, **70**, 307, 347 (1925).

[5] Dufraisse, *Rev. gén. caoutchouc*, **9**, 4 (1932); RUBBER CHEM. & TECH., **6**, 157 (1933).

[6] Cotton, *Trans. Inst. Rubber Ind.*, **6**, 487 (1931).

[7] Busse, *Ind. Eng. Chem.*, **24**, 140 (1932); RUBBER CHEM. & TECH., **5**, 164(1933).

[8] Dogadkin and Pantschenkow, *loc. cit.*

[9] Pummerer and Miedel, *Ber.*, **60**, 2148 (1927); RUBBER CHEM. & TECH., **1**, 163 (1928).

[10] A work of Gorter, cited by Bruni and Pelizolla, *India Rubber J.*, **63**, 415 (1922).

[11] Kemp, Bishop, and Laselle, *Ind. Eng. Chem.*, **23**, 1444 (1931); RUBBER CHEM. &. TECH., **5**, 51 (1932).

[12] Temple, Cadwell, and Mead, *Ind. Eng Chem., Anal. Ed.*, **3**, 377 (1930); RUBBER CHEM. & TECH., **4**, 126 (1931).

[13] Bruni and Pelizolla, *India Rubber J.*, **63**, 415 (1922).

[14] Dogadkin and Pantschenkow, *loc. cit.*; Dogadkin and Lawrenenko, *Kautschuk*, **4**, 97 (1933); RUBBER CHEM. & TECH., **6**, 436 (1933).

[15] Dogadkin and Pantschenkow, *loc. cit.*

[Reprinted from India Rubber Journal, Vol. 87, No. 8, pages 207–209, February 24, 1934, and comprising an abridged translation, without illustrations, of an article in Kautschuk, Vol. 9, No. 12, pages 182–184, December, 1933, and Vol. 10, No. 1, pages 4–7, January, 1934.]

The Russell Effect with Rubber

A. van Rossem and J. H. E. Hessels

National Rubber Institute, Delft, Holland

Introduction

Russell Effect is the name given to the action which many inorganic and organic substances, especially after exposure to light, exhibit in producing an image on a photographic plate in the dark. J. W. Russell (1897–1908) showed the effect to be due not to radiation, but to evolution of gaseous products, apparently hydrogen peroxide, and found that rubber showed this effect after exposure to light. van Rossem and Dekker (*Ind. Eng. Chem.*, **18,** 1152 (1926)) and Busse (*Ind. Eng. Chem.*, **24,** 140 (1932)) have also investigated the Russell effect of raw rubber. The present experiments were made (1) to find out whether the Russell effect will detect the first stages of oxidation or a tendency to oxidation in raw rubber, and (2) to study the Russell effect of vulcanized rubber, since it might prove useful for detecting incipient oxidation. Though the investigation has shown that the Russell effect is of little value as a test for the early stages of oxidation, the observations made are sufficiently important to warrant description.

Method

Very sensitive photographic plates (H. and D. 1400) were used. The edges of the rubber specimen were covered with tinfoil to prevent the image being diffused around the edges (apparently due to diffusion of the active gas). The specimens were usually laid directly on the plate, but tacky samples were either French-chalked or placed over openings in a celluloid sheet covering the plate. The whole was kept in darkness for 17–18 hours, and the plate then developed and fixed.

First Experiment

Various raw and vulcanized rubbers were subjected to:

(*a*) 3 to 5 hours' exposure to day or sunlight;
(*b*) 3 to 30 minutes' exposure to a Heraeus quartz mercury vapor lamp;
(*c*) 3 to 30 minutes' exposure to a Kelvin, Bottomley, and Baird Fugitometer (arc).

After the daylight exposure the raw rubber samples differed considerably in the intensity of the Russell effect, but after exposure to ultra-violet (mercury vapor) light they all gave strong images of about equal intensity. The latter result was shown to be due to the formation of hydrogen peroxide and/or volatile peroxides from an ozonide produced on the rubber surface by the ozone formed around the ultra-violet lamp. Consequently, such ultra-violet lamps are unsuitable for experiments on the Russell effect. The arc gave results in fair agreement with sunlight, but experiments with it were not continued, daylight being adopted as standard.

Behavior of Different Kinds of Raw Rubber

Various samples were exposed outdoors for 3 and 5 hours and then tested, previous tests having shown that unexposed samples produced no effect. The samples of

first latex (smoked) sheet produced a strong Russell effect, the first latex crepes only a weak effect, and hard fine Para and dried latex films no effect. The following questions now arose:

1. *Is Exposure to Light Really the Cause of the Russell Effect with Sheet?*—The fact that the effect was produced even by exposure on a cloudy day, and that traces of ozone are always present in the air, cast doubt on this point. It was shown, however, by two methods that the light is really responsible:

(*a*) Exposure for 5 hours during evening or night gave no Russell effect.

(*b*) Exposing in a closed box with a glass or quartz lid gave the same effect as exposure with free access of air. This test showed also that ultra-violet rays have no great activity in producing Russell effect (this confirms Schmutz, Nelson, and Stutz, *Ind. Eng. Chem.*, **17**, 1138 (1925)).

2. *Why Do Sheet, Crepe, and Para, and Dried Latex Differ?*—Samples of sheet varied considerably, some showing strong Russell effect, while six 15-year-old samples showed little or none. As the latter had lost the characteristic smoky smell, several sheet samples were examined for the Russell effect and smell, these properties being found to run parallel. Moreover, progressive acetone extraction gradually reduced the Russell effect as well as the smell. Hence it follows that in first latex sheet the Russell effect arises from the smoke components, and not from the rubber itself.

The only plausible explanation of the fact that hard fine Para gives no Russell effect seems to be that it is prepared with a different kind of smoke from that used for sheet.

Busse (*loc. cit.*) considered that Para and sprayed-latex rubber contain substances that decompose the peroxides formed during exposure, because adding 25 per cent of sprayed rubber to sheet destroyed the Russell effect. The present authors, however, could not confirm this observation. Moreover Busse's view that the serum components decompose the peroxides is rendered doubtful by the fact that dipping first latex sheet into a solution of serum components does not influence its Russell effect.

The Russell effect enables smoked sheet and hard fine Para to be distinguished after mastication or even in solution, which cannot be done by chemical analysis. Masticated sheet or dried films from benzene or naphtha solutions of sheet (masticated or unmasticated) all give the Russell effect, while similar preparations of hard fine Para do not.

As it was thought that the variable behavior of first latex crepes might be connected with their varying tendency to develop tackiness, four different samples were exposed for 1, 4, 8, and 24 hours to summer sun. The sample which gave the strongest Russell effect, however, developed much less tackiness than one of the other samples, showing that the relation between the tendency to develop tackiness and the Russell effect is not close enough to enable practically useful conclusions to be drawn from the latter.

Acetone Extraction

Though acetone extraction reduced the Russell effect of sheet, a sample of crepe after acetone extraction and exposure to light showed a strong tendency to tackiness and a strong Russell effect.

In further comparative tests sheet and crepe were acetone-extracted for 10 hours, and then exposed to sunlight for 1, 2, 3, 5, and 8 hours. The Russell effect from the extracted sheets, though increasing somewhat with the time of exposure, was

always less than that of the unextracted sample exposed for 3 hours. The extracted sheets showed no tackiness after 8 hours' exposure. The unextracted crepes all showed a weak Russell effect but no tackiness, while the extracted crepes showed an increasing Russell effect and tackiness with increasing time of exposure.

van Rossem and Dekker (*loc. cit.*) found that the acetone extract of crepe after 2 hours' exposure to light contained peroxides. The extracts of crepe, sheet, Para, and dried latex have now been found to give strong Russell effects, and dipping crepe in a solution of its own acetone extract causes it to show the effect strongly.

The curious fact that the acetone extracts of crepe and Para show the Russell effect, while the rubbers themselves do not, does not seem to be due to the state of distribution of the extract in the rubber, since mastication and solution do not influence the Russell effect, but is probably due to the small concentration (3 per cent) of the extractable matter in the rubber.

Influence of Heating on the Russell Effect

Pieces of first latex sheet after exposure to the sun were heated for 30 minutes at 20°, 30°, 50°, 70°, 80°, 90°, and 100° C. Those heated to 70° C. or below all gave an equally strong Russell effect, but those heated to 80° C. or above gave a much weaker effect, showing that the gaseous products causing the effect are either decomposed or driven off between 70° and 80° C. Similar experiments with the same rubber after exposure to ozone (instead of light) showed a gradual weakening of the Russell effect from 36° C. upward, the greatest weakening being between 50° and 60° C. It is concluded that the volatile peroxidic products formed under the influence of ozone are definitely different from those formed in sunlight.

Influence of Antioxidants

Experiments were made with *m*-dinitrobenzene and hydroquinone, which Leon and Lister (*J. Soc. Chem. Ind.*, **46**, 220T (1926)) have found to retard the oxidation of raw rubber, and with sodium bisulfite. Untreated samples of first latex sheet and samples that had been dipped in benzene and in 2 per cent solutions of dinitrobenzene in benzene and of hydroquinone and sodium bisulfite in water, were exposed to light and then tested. Hydroquinone and dinitrobenzene did not affect the Russell effect, but sodium bisulfite considerably reduced its intensity. The weak Russell effect of crepe, however, cannot be ascribed to the use of sodium bisulfite in its preparation, because dried latex containing no bisulfite likewise shows no Russell effect. Sodium sulfite does not influence the Russell effect.

Behavior of Masticated, Compounded, and Vulcanized Rubber

Both first latex sheet and crepe, vulcanized for 15, 30, or 45 minutes at 147° C. in a mixing of rubber 100, sulfur 5, diphenylguanidine 1, and zinc oxide 3, gave extremely weak Russell effects, the difference between the two rubbers having disappeared. Tests were accordingly made to find why the Russell effect of the sheet had almost disappeared.

(*a*) Samples of sheet, both masticated and unmasticated, were heated in moulds under vulcanizing conditions. After 3 hours' exposure to light they showed Russell effects similar to the untreated sheet, proving that heating alone is not responsible for the decrease in the Russell effect.

(*b*) Samples of sheet were tested: (1) after mastication; (2) masticated and compounded with sulfur, zinc oxide, and diphenylguanidine (proportions as above); (3) as (2) then vulcanized 30 minutes. After 3 hours' light exposure sample (1) was similar to unmasticated rubber, but (2) and especially (3) were much weaker.

To find out why compounding so greatly reduced the Russell effect, first latex sheet was mixed with each ingredient separately, with the following results:

	Russell Effect
Masticated	Normally strong
100 rubber and 3 zinc oxide	Normally strong
100 rubber and 1 diphenylguanidine	Normally strong
100 rubber and 5 sulfur	Rather weak
100 rubber and 3 zinc oxide, 1 diphenylguanidine, and 5 sulfur	Very weak

Similar results were obtained by dusting the masticated rubber with the various materials. It is seen that only the combination of all the ingredients seriously weakened the Russell effect. Mixings with various combinations were then tested:

	Russell Effect
100 rubber, 5 sulfur, 1 diphenylguanidine	Very weak
100 rubber, 5 sulfur, 3 zinc oxide	Rather weak
100 rubber, 1 diphenylguanidine, 3 zinc oxide	Strong
100 rubber, 5 sulfur, 1 diphenylguanidine, 3 zinc oxide	Weak

The sulfur-diphenylguanidine combination was the most active, evidently owing to the formation of a chemical compound that decomposes peroxides. Dusting with sulfur and diphenylguanidine after exposure to light, however, did not influence the Russell effect, showing that this compound is formed only during exposure to light and air. Tests with other accelerators (hexamethylenetetramine, triphenylguanidine, thiocarbanilide, mercaptobenzothiazole, and tetramethylthiuram disulfide) showed that triphenylguanidine and hexamethylenetetramine behaved like diphenylguanidine. Mercaptobenzothiazole, alone among the accelerators, caused the complete disappearance of the Russell effect. As a mixture of sulfur and diphenylguanidine forms mercaptobenzothiazole when heated (Bruni and Levi, *Chem. Zentr.*, **1924**, I, 2,366), the effect of sulfur plus diphenylguanidine on the Russell effect may be due to the formation of mercaptobenzothiazole during exposure to light. On the other hand, outdoor exposure of a benzene solution of diphenylguanidine and sulfur in a quartz vessel during the whole month of August failed to produce recognizable traces of mercaptobenzothiazole. The mode of reaction of diphenylguanidine and sulfur that results in weakening of the Russell effect therefore remains unsettled.

Vulcanized rubbers of various compositions all showed a very weak Russell effect. Stocks containing diphenylguanidine showed the weakening already after mixing, but with sulfur alone the uncured stock gave a fairly strong Russell effect, and the weakening was evident only after vulcanization.

Badly overcured rubbers and rubbers aged for 48 hours in a bomb at 60° C. under 20 atmospheres' pressure of oxygen showed only a very weak Russell effect. This indicates that the Russell effect is not suitable for detecting incipient oxidation or a tendency to oxidation (overvulcanization) in vulcanized rubber.

Vulcanized rubber exposed to ozonized air (even less than 0.01 per cent ozone content) showed a very strong Russell effect.

Summary

(1) The Russell effect from raw rubber, after exposure to light and air, depends on three factors: (*a*) *smoke components:* smoked sheet shows a strong Russell effect owing to the presence of these components; Para does not because it is prepared with a different kind of smoke; (*b*) *tackiness:* most crepes show little Russell effect, but prolonged exposure after acetone extraction causes concurrent

increases in both the Russell effect and tackiness; (*c*) *acetone extract:* the extract shows a strong Russell effect, but this is scarcely apparent when it is present in the rubber.

(2) The gaseous products that cause the Russell effect are decomposed or driven off at 80° C.

(3) These gaseous products are not the same as those formed by treatment with ozone.

(4) Antioxidants for raw rubber do not affect the Russell effect, but sodium bisulfite weakens it.

(5) Mastication or mixing with sulfur alone has little effect, but mixing with diphenylguanidine, triphenylguanidine or hexamethylenetetramine plus sulfur, or with mercaptobenzothiazole alone, considerably weakens the Russell effect.

(6) Vulcanized rubber (normally or overcured, or oxidized by aging) shows a very weak Russell effect; this effect therefore will not detect incipient oxidation or a tendency to oxidation.

(7) Quartz mercury vapor lamps are not suitable for experiments on the Russell effect, because the results are complicated by the ozone formed around them.

(8) Ozone, even in very low concentrations (0.01 per cent or less), causes a strong Russell effect in both raw and vulcanized rubber.

[Translated for Rubber Chemistry and Technology from Revue Générale du Caoutchouc, Vol. 10, No. 97, pages 17–20, December, 1933.]

The Electro-Deposition of Rubber on a Zinc Anode

B. Dogadkin and D. Sandomirsky

INSTITUTE OF THE RUBBER INDUSTRY, MOSCOW

Certain authors, among whom Klein[1] and Sheppard[2] in particular should be mentioned, have more than once pointed out that the rubber film which is formed on the anode, when rubber is deposited from latex by electrophoresis, is completely saturated with serum and has no influence on the electro-conductivity of the system. This fact makes it possible to obtain layers of rubber of any desired thickness. In the course of verifying this phenomenon, we became convinced that it is true only when the composition of the bath as well as the character of the electro-chemical phenomena taking place at the anode conform

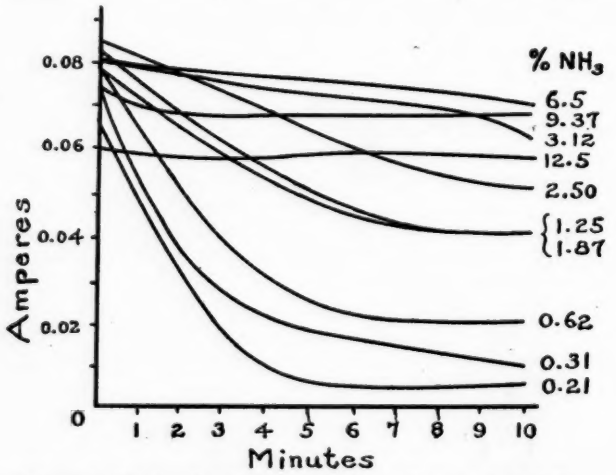

Figure 1—Diminution in Intensity of the Current during Deposition on Zinc in the Presence of Ammonia. Values on Curves Represent the Percentages of Ammonia

to certain conditions and bear certain relations to one another. By way of illustration we believe it is advisable to describe some experiments in detail.

When electro-deposition takes place on a zinc anode in preserved latex containing about 31 per cent of total solids, it is observed that as the operation proceeds there is a very sudden drop in the strength of the current passing through the bath, as a result of which the rate of deposition of rubber likewise diminishes. After the current has continued for two or three minutes, the deposition practically ceases. The thickness of the layer of rubber obtained under these conditions does not exceed 0.1 mm., which is a serious obstacle to the commercial application of this process.

Experiments carried out with different voltages at the anodes have shown that this factor does not have a very serious effect on the character of the operation.

For this reason, we give only the results of experiments in which the electro-deposition was carried out at 8 volts on zinc anodes having an area of 20 sq. cm. The cathodes were of carbon.

At the same time it was found that the character of the operation depends to a great extent upon the alkalinity of the bath, *i. e.*, upon the ammonia content of the latex. This is shown in Fig. 1. The original latex contained 0.2 per cent of ammonia. The addition of this substance to the bath, in addition to increasing the readings of the ammeter, is followed by a straightening out of the curve which represents the lowering of the strength of the current during the particular time. If the ammonia content is greater than 3 per cent, the diminution in the strength of the current is almost insignificant, and the rate of the deposition of

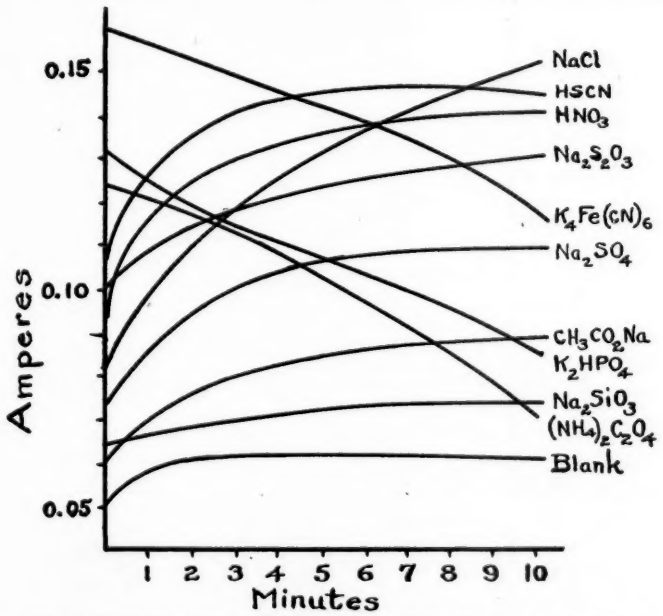

Figure 2—Diminution in the Intensity of the Current during Deposition on a Zinc Anode Surrounded by Gypsum, in the Presence of Different Electrolytes

the rubber is practically constant. In this case a layer of rubber of the desired thickness can be obtained.[3]

The sudden lowering of the current strength, which increases in proportion to the electrophoresis of rubber from a weakly alkaline latex, can be explained by the phenomenon of the anomalous polarization of the zinc anode. Müller[4] has called attention to this phenomenon in the case of the electrolysis of solutions of sulfates and phosphates containing ammonia at concentrations above 0.01 normal. In neutral solutions of these salts no abnormal polarization is observed at the zinc anode. This polarization is related to the formation at the anode of a deposit of insoluble salts. Nevertheless, the probable importance of the electromotive force of polarization under the conditions described would not have been capable of bringing about a lowering of the current strength. Furthermore tests of electrolysis with ammonia in the concentrations given did not lower the current strength

in the circuit. A soft layer of zinc hydroxide was formed on the anode, and this layer covered only a portion of the surface of the electrode.

In order to determine the influence that the phenomena at the anode have upon the electrophoresis of rubber, some experiments were made on the deposition of rubber on zinc plates covered with plaster or separated from the latex by a Schott glass filter plate. Before being immersed in the bath, the plaster-covered electrode was moistened with distilled water. In other respects, the experiments were carried out under the same conditions as were the preceding experiments. It was found that, independent of the alkalinity of the medium and of the ammonia content of the latex, in all cases with low current densities (0.0015–0.0004 ampere

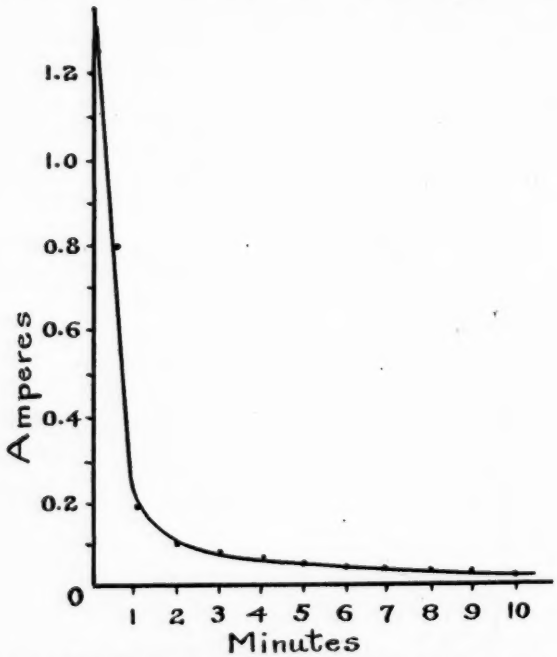

Figure 3—Diminution in the Intensity of the Current during Electrolysis of a Solution Containing 5 Per Cent Casein and 2 Per Cent of Ammonia

per sq. cm.) the strength of the current did not diminish during the electrophoresis, and the rate of the deposition remained practically constant (Fig. 2). By using a higher current density (0.01 ampere per sq. cm.) a definite lowering of the current was observed within 4 or 5 minutes. This diminution can be explained by an increase in the specific resistance of the film as a result of electro-osmotic phenomena. The electrochemical phenomena which take place at the zinc electrode, other than the formation of the layer of rubber, are not in themselves harmful to the mechanism of electrolytic deposition. In the same way it may be assumed that the layer of rubber formed at a certain distance (3–8 mm.) from the zinc electrode has no influence on the electro-conductivity of the bath.

The process involved in the electrolytic deposition of rubber directly on zinc must be regarded not as a simple migration and discharge of latex globules on the

surface of the anode, but as a process connected with the electro-chemical phenomena which take place simultaneously on the electrode. The character of the phenomena determines the structure of the deposit, and consequently the progress of the operation. In immediate proximity to the anode, the liquid becomes acid up to a certain point, which in turn brings about dehydration of the protein shells of the transported globules of latex, and this results in a more extensive coagulation of the film. The composition of the film differs from that determined by the composition of the bath as a result of solution of zinc at the anode. The concentration of zinc ions in immediate proximity to the anode is very great, and as a result of the reciprocal action of these ions and of organic substances of a colloidal character which are contained in the latex, a compact non-conducting deposit forms on the zinc anode. That this is exactly what takes place has been proved by an experiment on the electrolysis of ammonia to which a certain quantity of

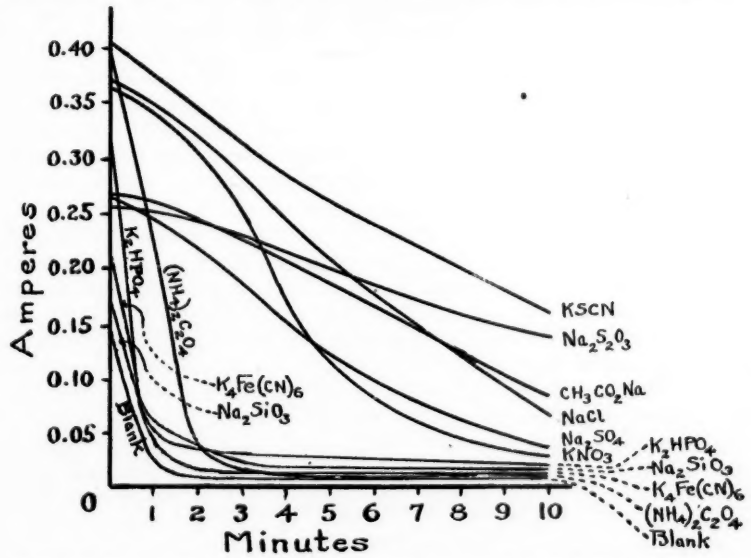

Figure 4—Diminution in the Intensity of the Current during Deposition on a Zinc Anode, in the Presence of Various Electrolytes

casein was added. In this case too a very sudden lowering of the current strength was observed (Fig. 3), and the electrode became covered with a thin, decidedly compact layer, which was a mixture (or absorbed combination) of zinc hydroxide and casein. Overvoltage of the electrode in the case of electrolysis in the presence of dispersed colloidal substances is also known.

The influence of the ammonia added to make the latex more alkaline must be studied as much from the point of view of the effect of this substance upon the phenomena at the anode, as from the point of view of its effect upon the structure of the film of rubber deposited. In a weakly alkaline bath, there is formed, for reasons mentioned above, a compact and non-conducting film of rubber and insoluble zinc salts, combined by adsorption with the proteins and other substances of the serum. In a sufficiently alkaline bath (more than 2 per cent of ammonia), the phenomenon by which the liquid reaching the anode becomes acid is paralyzed by the surplus of hydroxide ions. The peptizing action of alkalies leads to the

formation of a layer of soft rubber of good conductivity. Evidently the concentrations of ammonia described prevent the formation at the anode of a deposit of insoluble zinc salts, while the zinc oxide which is formed at the anode reacts with the ammonium hydroxide, with formation of soluble zincates.

The action of different salts added to the bath can be explained in a similar way. The following salts were examined: sodium chloride, potassium nitrate, sodium phosphate, potassium thiocyanate, sodium acetate, sodium thiosulfate, sodium sulfite, potassium ferrocyanide, dipotassium phosphate, and ammonium oxalate. Their concentration in the latex was 0.1 normal. Fig. 4 shows the results of these experiments. As is evident from this figure, the salts can be divided into two groups, according to their effect. The salts of the first group, namely sodium sulfite, potassium ferrocyanide, dipotassium phosphate, and ammonium oxalate do not have any notable influence on the course of the phenomenon. The diminution in the strength of the current occurs as suddenly as in the case of the electrophoresis of the original latex which contained no ammonia. The salts of the second group, sodium chloride, potassium nitrate, sodium sulfate, potassium thiocyanate, sodium acetate, sodium thiosulfate retard to a perceptible degree the diminution in the strength of the current. In the presence of these salts a layer of rubber of considerable thickness is formed. The salts of this group contain anions which, contrary to anions of the first group, form with the zinc, easily soluble compounds. This fact determines the course of the phenomenon at the anode during electrophoresis. In the presence of salts of the first group the zinc electrode becomes covered with a layer of insoluble compounds. In the presence of salts of the second group the phenomenon taking place at the anode results in the formation of soluble compounds, which diffuse into the interior of the rubber film. This was proved by the results obtained in determinations of the quantity of ash in the films of deposited rubber as shown in the table. As is seen in this table, the nature of the effect of any particular anion in relation to the course of electrolytic deposition of the rubber coincides with the solubility of the compound of the anion with zinc, and its content in the rubber film. Similar results were obtained in cases where the deposition took place on zinc electrodes covered with plaster or compressed powdered glass. As has already been said, no diminution in the strength of the current was observed in this case during the electrophoresis. On the contrary, for two or three minutes a definite increase in the strength of the current was observed, which may be explained by infiltration into the plaster of latex serum containing electrolytes. This increase becomes more pronounced if salts of the second group are added to the bath (Fig. 2). In the case where salts of the first group are added to the bath, there is an appreciable diminution in the strength of the current, and in the diminution in the rate of the deposition of the rubber. This phenomenon must be regarded as the result of processes at the anode which in the presence of the salts named take place directly on the zinc.

We believe that it might be of interest to mention that the deposition of rubber on the porous diaphragms surrounding the zinc electrode takes place under conditions somewhat different from the point of view of the structure of the field of forces. The material of the diaphragm insulates an important part of the electrode, and the effective density of the current at the surface of the diaphragm is noticeably greater than it is during the direct deposition on a zinc plate. This circumstance cannot fail to have a certain influence on the structure and physical properties of the rubber film, particularly on its penetration by gases and on its conductivity. Further experiments will prove whether this is actually the case.

Conclusions

1. During the electrophoresis of rubber on a zinc anode in a weakly alkaline latex (concentration of ammonia less than 2 per cent), there is a sudden drop in the current, and as a result a diminution in the rate of deposition of the rubber. In a strongly alkaline bath, the rate of deposition remains practically constant.

2. The addition to the latex of salts the anions of which give soluble compounds with zinc diminishes to a marked degree the drop in the current strength.

3. The action of salts and alkalies is explained by the nature of the phenomenon at the anode and the structure of the film of rubber deposited.

4. The electrolytic deposition of rubber on zinc electrodes surrounded by a diaphragm of plaster or of glass takes place at a practically constant rate, irrespective of the concentration of the alkalinity in the latex. A diminution in the rapidity of the deposition of rubber still takes place upon the addition to the bath of salts the anions of which form insoluble compounds with zinc.

In conclusion the authors wish to express their very deep gratitude to the Director of the Institute, Dr. L. G. Landau, for the interest which he has taken in their work.

TABLE I

PERCENTAGE OF ASH IN RUBBER FILMS DEPOSITED FROM LATEX IN THE PRESENCE OF DIFFERENT SALTS

Electrolyte	Percentage of Ash in the Rubber Film	Solubility of the Salt in Grams per 100 Cc. of Water at Temperature Indicated (Landolt Indicator)	
Group I			
Potassium ferrocyanide	1.8	Insoluble	
Dipotassium phosphate	1.9	Insoluble	
Sodium silicate	1.7	Insoluble	
Ammonium oxalate	3.1	0.00064	17.92°
Group II			
Sodium chloride	4.1	78.4	20°
Sodium acetate	3.9	40.0	25°
Potassium thiocyanate	4.5	?	..
Potassium nitrate	3.1	33.7	18°
Sodium sulfate	3.9	36.6	25°
Sodium thiosulfate	4.1	?	..

References

[1] *Trans. Inst. Rubber Ind.*, **4**, 343 (1927).

[2] *Trans. Am. Electrochem. Soc.*, **52**, 47 (1927).

[3] The necessity of adding ammonia to the latex in order for the deposition of rubber to proceed in a normal way was mentioned by Budiloff in a paper which was published after the present work was completed (cf. *Kautschuk*, **9**, 20 (1933); RUBBER CHEM. & TECH., **6**, 422 (1933)).

[4] *Z. Electrochemie*, **2**, 755 (1905).

[5] Cf. Harkins and Adams, *J. Phys. Chem.*, **29**, 205 (1905).

[Reprinted from Journal of the Society of Chemical Industry, Vol. 53, No. 6, pages 43–47T, February 9, 1934.]

The Preparation of Chlorinated Rubbers from Latex. Hypochlorination and Chlorination Processes

G. F. Bloomfield and E. H. Farmer

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY, LONDON, S. W. 7

With the view of extending the field of application of rubber latex, it has been considered desirable to study the behavior of this material toward various chemical reagents. Owing to the colloidal nature of latex the choice of reagent is considerably restricted; acids and many salts (especially those of bivalent and tervalent metals) produce coagulation, while alkaline reagents may cause creaming and aggregation of the particles. It is known that with the aid of certain stabilizers (*e. g.*, saponin or casein) a stable acid latex may be obtained, but this is in general only stable over a limited range of p_H values and is not stable to heat; moreover the stabilizer itself is prone to attack by the chemical reagent introduced.

As would be anticipated from the foregoing considerations, the direct introduction of chlorine into latex immediately causes coagulation. Ellis and Boehmer (U. S. Patent 1,544,535) appear to have achieved some measure of success in chlorinating latex by using liquid chlorine under pressure, but the products obtained in different operations varied considerably in their properties.

It is known that hypochlorous acid in dilute aqueous solution is practically non-ionized and is consequently non-acidic; moreover, it can be readily obtained free from any substantial quantities of chlorine or of hydrochloric acid (Taylor, MacMullin, and Gammal, *J. Amer. Chem. Soc.*, **47**, 395 (1925); Bloomfield and Farmer, *J. Chem. Soc.* **1932**, 2062). Some modification of the method of preparation is necessary, since the reagent prepared by these workers contains calcium chloride, which is a latex coagulant. This is achieved by passing chlorine into sodium bicarbonate solution instead of into calcium carbonate suspended in water; the solution of hypochlorous acid so produced contains, in addition to the reagent, only sodium chloride and bicarbonate, and is therefore suitable for admixture with latex. The presence of ammonia in the latex is not objectionable, since ammonia is decomposed by hypochlorous acid with evolution of nitrogen ($5NH_3 + 3HOCl = 3NH_4Cl + 3H_2O + N_2$).

Hypochlorous acid is a reagent for the ethylenic linking, and it is to be expected that it will enter into combination with the rubber molecule by attaching itself to the unsaturated centers, so producing the isomeric additive products of the types:

$$[\cdots\text{CH}\cdot\text{CMeCl}\cdot\text{CH(OH)}\cdot\text{CH}_2\cdots]_n \text{ and}$$
$$[\cdots\text{CH}\cdot\text{CMe(OH)}\cdot\text{CHCl}\cdot\text{CH}_2\cdots]_n.$$

The product actually obtained is an almost insoluble yellow powder which does not lend itself to the separation of isomeric materials, but does correspond approximately in chlorine content to that required by the simple additive product $(C_5H_8,HOCl)_n$.

It is claimed that treatment of latex with small amounts of sodium hypochlorite yields after coagulation a tacky rubber (British Patent 333,391), and this is also found to be true when free hypochlorous acid is added in small amount. According to our experiments tackiness increases with increase in the proportion of hypochlorous acid until 15% of 1 mol of the reagent per rubber unit (C_5H_8) has been added; this tackiness subsequently diminishes with the employment of larger proportions of the reagent. A tack-free material is obtained when 30 per cent of one molecular proportion of hypochlorous acid has been added; with still higher proportions of the reagent the tendency of the product to crumble becomes increasingly apparent until at the stage represented by 85–90 per cent of 1 mol of the reagent, the product is directly isolable as a powder. The solubility of the hypochlorinated product in the common rubber solvents decreases rapidly with increase in the proportion of the reagent employed; moreover the chlorine content of these modified rubbers corresponds almost exactly to the amount of hypochlorous acid employed.

Treatment of latex with a proportion of hypochlorous acid in excess of 1 mol per C_5H_8 unit shows at once that the rubber molecule is capable of facile chlorination beyond the point corresponding to the mere additive saturation of its unsaturated centers. This property reveals itself as a notable characteristic of rubber, whether the latter comes to reaction in the form of latex or is employed in solution. This property, moreover, does not appear to be shared by common mono- and diolefinic substances—at any rate under the conditions of operation here employed—since reaction in these cases is usually limited to attachment of the reagent at the unsaturated centers and does not involve direct replacement of hydrogen by chlorine. This being the case, some doubt appears to rest on the assumption made above that the reaction between even one molecular proportion (or less) of hypochlorous acid and the rubber unit is entirely of an additive nature; and unfortunately owing to the intractability of the hypochlorination products in general, it is impossible to determine satisfactorily their hydroxylic contents or degrees of unsaturation, or to arrive at any valid conclusions concerning their degree of uniformity by employment of separative methods. The carbon and hydrogen contents of these materials, however, when taken in conjunction with the chlorine content, leave little room for doubt as to the preponderatingly additive nature of the first interaction between the reagent and the rubber molecule under the conditions here employed.

A maximum chlorine content of approximately 42 per cent is obtained when 4 mols of hypochlorous acid per rubber unit are used; with larger proportions of hypochlorous acid the excess of reagent remains unchanged. Products having a chlorine content between 28 and 42 per cent are all yellowish insoluble powders, the color becoming lighter as the chlorine content increases. The yellow color appears to owe its origin to serum substances, since much whiter products are obtained from 60 per cent centrifuged latex.

The products are stable in daylight at room temperature, but decompose on heating, the stability toward heat decreasing with increasing chlorine content. They are also stable toward cold water and aqueous alkali, but partial loss of halogen occurs on heating, the resultant brownish powders being more stable than their parent material toward heat. On heating the more highly chlorinated materials with organic bases at 120–150° C., loss of halogen becomes more complete, but the dark colored insoluble materials so obtained still retain some halogen; this behavior is comparable with the already known behavior of "rubber hydrochloride" toward similar reagents. The materials are attacked readily by sulfuric and nitric acids, the latter reagent yielding a yellow nitrogenous substance. Chlorination may be made to proceed still further by suspending the hypochlorinated material (in which hydrogen replacement has already gone far) in carbon tetrachloride and leading in

chlorine at 80° C.; the most highly chlorinated material so obtained is a white insoluble powder containing 55–60 per cent of chlorine.

Since hypochlorous acid reacts with latex without causing coagulation, it was thought that it might be possible to produce this reagent satisfactorily *in situ*, by leading chlorine gas into latex containing excess of sodium bicarbonate. This process proved successful, and chlorinated rubbers (in the first stage largely hypochlorinated) of widely different chlorine content may be obtained at will by using a predetermined amount of chlorine. The products are in all respects similar to those obtained previously, but the chlorination proceeds further, a maximum chlorine content of about 45 per cent being reached. Similar products are obtained by the direct chlorination of stabilized acid latex, or of latex containing only small quantities of sodium bicarbonate, carbonate or hydroxide, or by further chlorination in acid suspension of materials of low chlorine content, but the materials so obtained are less homogeneous and less stable toward heat.

It is well known that in processes for the manufacture of chlorinated rubbers from rubber solutions, unstable products are obtained if the chlorination is carried out below 80° C. Unfortunately for the production of more stable materials by employment of hypochlorous acid or aqueous chlorine at higher temperatures, our experiments show that latex cannot be directly chlorinated at temperatures above 50° C., even in the presence of bicarbonate or of stabilizers without the occurrence of coagulation. The temperature may, however, be raised at any time after one whole molecular proportion of hypochlorous acid has entered reaction, and the chlorination may then be completed at 80–100° C. The resultant materials are pure white or pale cream powders which vary considerably in chlorine content and in other properties from batch to batch of latex, although quite uniform products are obtained from any one batch. One particular latex yielded a white powder which was readily soluble in chloroform, acetylene tetrachloride, cyclohexanone, diacetone alcohol, and allied solvents, but all other batches of latex tested yielded insoluble yellowish powders; moreover this particular latex also gave after an interval of two months only insoluble products.

The results obtained from a series of chlorinations carried out by passing chlorine gas into a number of different latices containing various added substances indicate that some component of the serum (most probably a protein) catalyzes in some unknown way the chlorination process. In order that a chlorination product shall be soluble, a chlorine content exceeding 50 per cent is necessary, and this figure is obtained only in the presence of this (catalyzing) serum substance. The catalyst may be conveniently introduced in the form of added serum—either serum specially expressed from a further quantity of latex, or separated in larger-scale centrifuging operations: the quantity to be added depends entirely on the age of the serum. The active serum component may be obtained in concentrated form by evaporation (preferably *in vacuo*) of serum, but the activity appears to be lost more rapidly when concentrated, and indeed various specimens of dried serum kindly supplied by Prof. G. Bruni, Dr. H. P. Stevens, and the London Advisory Committee for Rubber Research (Ceylon and Malaya) possessed little or no catalytic activity. The addition of active serum to any latex (including centrifuged latex), enables soluble chlorinated products to be obtained. Other added protein matters (glue, gelatin, casein) enable somewhat soluble products to be prepared, but the best results are obtained with serum.

The highly chlorinated rubbers obtained by these means, like the chlorinated materials previously obtained, are unstable to heat, vigorous decomposition setting in at 110° C. Some specimens are so unstable as to evolve hydrogen chloride freely *in vacuo* at room temperature. Heating with water at 100° C., effects some

degree of stabilization, but this procedure involves a considerable reduction in the chlorine content. With concentrated hydrochloric acid chlorine is evolved, but there is no substantial change in the ultimate chlorine content or in the solubility; phosphorus trichloride and oxychloride are without appreciable action. The highly chlorinated rubbers are readily attacked by both sulfuric and nitric acids, but with alkalis and organic bases they behave similarly to the rubber chlorohydrins previously described.

The differences in stability and solubility between chlorinated rubbers obtained from latex as above, and those obtained by the action of chlorine or of hypochlorous acid on rubber solutions, are very striking and point to a deep-seated difference in the mechanism of reaction in aqueous dispersion and in solution. That these differences are mainly or entirely due to the extensively hydroxylated condition of the molecules in one group of derivatives and to their relatively hydroxyl-free condition in the other appears unlikely in view of the fact that chlorinated derivatives may be obtained by the action of hypochlorous acid on rubber solution, which although extensively hydroxylated, as determined by the Zerevitinov method, are yet soluble (unpublished work).

A method of preparing readily soluble chlorinated rubbers by chlorination of oxidized latex in the presence of sodium dibutylnaphthalenesulfonate has been recently described (British Patent 390,097), but oxidized latex subjected to chlorination by the process developed above yields an insoluble material unless serum or "skim" is added, in which case a product of slightly enhanced solubility is obtained. The small improvement in solubility obtained, however, is not sufficient to justify the time and the labor involved in the oxidation process.

Chlorination of vulcanized latex yields a white powder containing sulfur which is partly soluble in the usual solvents for rubber.

In view of the inconsistency of the results obtained with different specimens of imported (more or less aged) latex, and the interesting influence of serum components on the chlorination process, it appears desirable for further work on the above-described lines to be carried out with fresh latex on the rubber estates.

Experimental

Preparation of Hypochlorous Acid.—1000 cc. of water containing 100 grams of sodium bicarbonate were chlorinated at 0° C., with stirring, until a concentration of approximately 1.5 per cent of hypochlorous acid had been reached (determined by titrating the iodine liberated from potassium iodide with standard thiosulfate). The concentration of the solution was then determined accurately and the quantity required to react with a given bulk of latex calculated.

Addition of Hypochlorous Acid to Latex

I. *Addition of One Molecular Proportion of Hypochlorous Acid per* C_5H_8 *Unit.*—1000 cc. of 1.58 per cent hypochlorous acid (5 per cent excess above theory) were run slowly into 57 cc. of 34% ammonia-preserved latex diluted to 200 cc. with water, the mixture being kept stirred and ice-cooled. No hypochlorous acid remained after 16 hours and a finely divided pale yellow precipitate had settled to the bottom of the vessel; this precipitate passed through a filter-paper but was retained on a porous tile as a fine dry powder. On acidifying the suspension, however, the precipitate became coarser and could then be retained on a filter-paper. The material was accordingly filtered off, was well washed and dried, and was obtained as a light, fine pale yellow powder. Yield: 33.5 grams (95 per cent of theory assuming a simple additive process to have taken place).

The powder was insoluble in organic solvents, but swelled considerably in benzene hydrocarbons, esters, carbon disulfide, cyclohexanone, and allied solvents. It had the anticipated chlorine content of a simple chlorohydrin (found: C 53.2, H 6.35, Cl 29.8%; C_5H_9OCl requires C 49.9, H 7.48, Cl 29.4%). On heating, decomposition occurred at 130° C. It was only partly attacked by acid dichromate solution and by acetic anhydride, both reagents, as also sulfuric acid, causing charring. Concentrated nitric acid attacked it readily, and on dilution of the product a nitrogenous acid of unknown composition was precipitated. When heated with water or aqueous or alcoholic alkali, loss of halogen occurred and the powder darkened in color; when heated with pyridine or aniline at 120–150° C., a swollen reddish brown mass was obtained, which dried to a brown insoluble powder still containing some halogen.

II. *Addition of Smaller Proportions of Hypochlorous acid.*—The additions were carried out as described above, using 2, 5, 10, 15, 20, 25, 50, 70, and 90 per cent of 1 mol. of hypochlorous acid per C_5H_8 unit respectively. Acidification of the reaction product yielded, in all cases except the last of the series, rubber-like coagula displaying progressive darkening in colors; in the last addition a rather coarse dark yellow powder was obtained. The first four materials were tacky, the next was rather less tacky, while the materials made by employing 25 per cent or more of 1 mol of the reagent were non-tacky. All of the products swelled in solvents, but only the first four of the series dissolved to any extent, and these were difficultly soluble, indeed, only the first dissolved at all readily. The chlorine contents of the products corresponded almost exactly to the amounts of hypochlorous acid employed; thus for 25 per cent addition, Cl = 7.9% (corresponding to the effective union of 27% of 1 mol of HOCl per C_5H_8 unit); for 50 per cent addition, Cl = 15.3% (corresponding to 52% of 1 mol of HOCl); for 70 per cent addition, Cl = 20.5% (corresponding to 70% of 1 mol of HOCl). When thoroughly dry, the last three materials of the series (50, 70, and 90%) crumbled to coarse brown powder.

III. *Treatment of Latex with Excess of Hypochlorous acid.*—Twenty cc. of 34 per cent latex were treated with 1760 cc. of 1.2 per cent hypochlorous acid (4 mols). A small excess of hypochlorous acid remained after two days, and this was destroyed by careful addition of ammonia. The product isolated after acidification of the reaction mixture consisted of 14 grams of a pale yellow powder indistinguishable in ordinary properties from the material described under I (found: Cl 41.5%; C_5H_9OCl requires Cl 29.4%; $C_5H_8OCl_2$ requires Cl 45.8%).

IV. *Preparation of Chlorinated Materials by Direct Chlorination.*—Thirty-four per cent latex was mixed with 10 times its volume of 10 per cent aqueous sodium bicarbonate and chlorinated with ice-cooling (temperature between 0° and 10°) until chlorine was no longer freely absorbed. After 24 hours the excess of reagent was decomposed with ammonia and the product isolated by acidification and filtration. An insoluble cream-colored powder was obtained which had a rather higher chlorine content than any of the previously described materials (found: Cl 45.8%; $C_5H_8OCl_2$ requires Cl 45.8%. The coincidence of experimental and calculated values is probably fortuitous). By stopping the chlorination earlier, intermediate products were obtained possessing properties similar to those of the materials described under I, II, and III.

V. *Treatment of 60 per cent Centrifuged Latex with Chlorine.*—Latex concentrated by centrifuging gave products of similar nature to, but much cleaner than, those obtained with more dilute latex. The cleanness of the product was doubtless due to the absence of serum impurities.

VI. *Further Chlorination of Hypochlorinated Materials.*—The material obtained under I was suspended in carbon tetrachloride, and chlorinated at the boiling point

of the solvent until hydrogen chloride ceased to be evolved. None of the material dissolved and on filtration a coarse white powder insoluble in all solvents was obtained (found: Cl 56.3%. $C_5H_7OCl_3$ requires Cl 56.2%).

The material obtained under III was similarly treated, and yielded a similar product to the above (found: Cl 59.1%).

VII. *Direct Chlorination of Latex.*—Chlorinated materials very similar to those described under IV were obtained by chlorinating casein-stabilized acid latex, or latex containing sodium carbonate (or hydroxide) instead of sodium bicarbonate. But all these new substances were probably mixtures of rubber derivatives in which chlorination had occurred to different extents. All were insoluble.

Since the material obtained by process IV was obtained as a powder which was not coagulated by heat or acid, it became apparent that the temperature could be raised after the completion of process IV and further chlorination carried out at 80–100° under acid conditions. (It is, of course, not possible to work in the presence of bicarbonate at this temperature, owing to the speed with which the bicarbonate is attacked.) Accordingly, latex to which sodium bicarbonate solution had been added (10 volumes of 5 per cent solution were found to be sufficient) was chlorinated at 0–10° C. very slowly until chlorine was freely evolved and the suspension had an acid reaction; then chlorine was passed in more rapidly and the temperature was raised gradually to 80–100° C. with continued stirring. Considerable thickening and frothing occurred in the latter process. When chlorine ceased to be absorbed the paste was filtered and from the first batch of latex treated in this way there was obtained a pure white, very fine powder (found: Cl 51.1%) which dissolved readily in chloroform, acetylene tetrachloride, cyclohexanone, methylcyclohexanone, cyclohexyl acetate, and diacetone alcohol, to give clear rather viscous solutions. This product lost hydrogen chloride *in vacuo* at room temperature and when subjected to heat it decomposed vigorously at 110°. Heating with water at 100° C. rendered it rather more stable (decomposition at 170° C.), but also rendered it insoluble; moreover, much of the chlorine was lost as was shown by the considerable proportion of free hydrochloric acid in the mother liquor. On heating with concentrated hydrochloric acid free chlorine was evolved, but the chlorine content of the material was not greatly changed by the treatment (found: 50.8%); toward phosphorus trichloride and oxychloride the substance had no apparent action, and toward other reagents it behaved exactly as described under I.

Unless the conditions specified above were closely adhered to, insoluble materials were obtained; thus neither the early stages nor the heating could be unduly hurried. Ice-cooling, however, could be dispensed with in the first part of the process.

No other specimen of latex tested gave a soluble chlorination product; three other specimens of Malay latex, a Java latex, and a 60 per cent centrifuged latex all gave white or yellow insoluble powders of lower chlorine content than above (found: Cl 47.3%, 43.7%, and 46.4% for three different preparations). Moreover after an interval of two months the original batch of Malay latex no longer gave soluble products.

The effect on the solubility of the chlorination product of adding various substances to the latex was systematically tested. The results are tabulated below.

It was apparent that the catalyst was a serum substance—probably a protein material. The quantity of added ("active") serum necessary to yield a soluble product was reasonably small; using skim, or serum expressed from coagulated latex, a quantity equal to half the volume of the latex to be chlorinated was in general sufficient.

Chlorination in the presence of a decreased proportion of bicarbonate, or under

acid conditions, yielded only insoluble materials, even in the presence of added serum.

VIII. *Chlorination of Oxidized Latex.*—Latex was oxidized with hydrogen peroxide as described by the I. G. Farbenindustrie (British Patent 390,097) but without addition of sodium dibutylnaphthalenesulfonate; sodium bicarbonate was then added to the product and the material subjected to the action of chlorine. In the presence of added serum slightly more soluble products were obtained, but without added serum the products were always insoluble.

IX. *Chlorination of Vulcanized Latex.*—Two specimens of vulcanized latex were chlorinated as in VI without addition of serum. Partly soluble white powders containing sulfur were obtained.

Specimen of Latex	Substance Added	Product
Malay 1[a]	Skim[b]	White, soluble
Malay 2	Skim	White, soluble
Malay 3	Skim	White, soluble
Malay 4	Skim	White, soluble
Java 1	Skim	White, soluble
60% centrifuged	Skim	White, soluble
Malay 1	Serum from Malay 1	White, soluble
Malay 3	Serum from Malay 2	White, soluble
60% centrifuged	Serum from Malay 1	White, soluble
Malay 1	Serum from Malay 1 evaporated to syrup	White, soluble
Malay 1	Quebrachitol	Yellow, insoluble
Malay 1	Na and Mg phosphates	Yellow, insoluble
Malay 1	Glue	White, dissolved in 3 days
Malay 1	Gelatin	White, dissolved in a week
	Casein	
Malay 1	Sodium oleate	White, insoluble
Malay 1	Deproteinized skim[c]	Yellow, insoluble
Malay 1	Skim, freed from heat-coagulable protein[d]	White, soluble
Malay 1	Dried serum (G. Bruni)	White, insoluble
Malay 1	Dried serum (H. P. Stevens)	White, dissolved in a week
Malay 1	Dried serum (London Advisory Committee for Rubber Research)	White, dissolved in a week

[a] Malay 1 was the latex which originally gave soluble materials.

[b] "Skim" was obtained by centrifuging 30% latex.

[c] "Deproteinized skim" was obtained by heating "skim" to 150° C. in an autoclave for 14 hours, under which conditions protein matter is broken down.

[d] Skim was acidified to permit the removal of residual rubber, after which it was again rendered alkaline and then heated to 60° to precipitate the heat-coagulable protein.

The authors are indebted to the Rubber Growers' Association, for whom this work was carried out, for permission to publish, and express their thanks to the members of the Modified Rubbers Research Committee for valuable advice.

[Reprinted from Journal of the Society of Chemical Industry, Vol. 53, No. 6, pages 47–48T, February 9, 1934.]

The Action of Hypochlorous Acid on Rubber

G. F. Bloomfield and E. H. Farmer

Imperial College of Science and Technology, London, S. W. 7

It has been previously observed that when rubber latex is treated with cold aqueous hypochlorous acid, the simple additive attachment of the hypochlorous acid molecule at the ethylenic center of each C_5H_8 unit of the rubber molecule may be accompanied by a considerable amount of substitutional chlorination (cf. preceding article). An analogous behavior has now been found to characterize the interaction of dissolved rubber (rubber solutions) with hypochlorous acid, but in this case marked differences in the properties of the reaction products become manifest. In the treatment of dissolved rubber some evidence of substitutional chlorination is directly apparent, even where the amount of hypochlorous acid does not exceed one molecular proportion per C_5H_8 unit, and considerable replacement of hydrogen by chlorine occurs when the reagent is present in excess of this amount; indeed, by using a suitable excess of the latter, it is possible to obtain chlorinated materials with a maximum chlorine content of 66 per cent. Now it is of practical importance to note that, whereas the chlorinated materials obtained from latex are characterized by a high degree of insolubility, the analogous materials from dissolved rubber are relatively soluble, and in the case of some of the more highly chlorinated materials are readily soluble in the ordinary solvents for rubber.

When hypochlorous acid in the proportion of 1 mol per C_5H_8 unit is added to a solution of rubber, a little gelatinous material invariably separates, irrespective of whether the rubber employed has been purified or not. This gelatinous material dries to an insoluble mass which contains a proportion of chlorine considerably in excess of that required for the simple chlorohydrin $(C_5H_9OCl)_n$; the product isolable from the mother liquor is correspondingly deficient in chlorine, but the sum of the chlorine in the two products accounts for the whole of the hypochlorous acid added. The analytical figures obtained for the second of these products show the chlorine-oxygen ratio to be somewhat higher than that to be expected for a simple chlorohydrin of formula $(C_5H_9OCl)_n$, and it is apparent that even in the simple case represented by the employment of 1 mol of the reagent for each C_5H_8 unit of the rubber, some substitutional chlorination (or possibly chlorine addition) occurs.* The product derived from the mother liquor is soluble when freshly precipitated, but when freed from solvent it rapidly becomes insoluble, brittle, and horn-like. This tendency to become insoluble, which is characteristic of a number of rubber derivatives, is inhibited by the presence of a trace of quinol; consequently it would appear to be due to some species of molecular aggregation or polymerization.

Proportions of hypochlorous acid in excess of 1 mol per C_5H_8 unit yield more highly chlorinated materials than the foregoing, but the nature of these is in some measure dependent on the solvent employed, since, owing to the insolubility of the earlier products in the particular solvent taken, precipitation may occur before the highest stage of chlorination is reached. A homogeneous soluble material

* Assuming that no chlorine addition occurs, about 30 per cent of the available chlorine in the hypochlorous acid supplied appears to be utilized in effecting substitutional chlorination.

obtained only when the solvent employed is chloroform; the product then has the highest chlorine content of any here prepared, but possesses nevertheless considerable hydroxyl content (8.5%). The empirical formula which corresponds most closely to the composition of this substance, while at the same time complying with the unitary (C_5H_8) method of rubber formulation, is $C_5H_6OCl_4$, but the agreement between the analytical figures and the calculated values is by no means exact.

Experimental

Preparation of Hypochlorous Acid.—A dilute aqueous solution of hypochlorous acid (about 1 per cent) was prepared by passing chlorine slowly into a cold, well-stirred suspension of calcium carbonate in water (50 grams per liter) (Taylor, MacMullin, and Gammal, *J. Am. Chem. Soc.*, **47**, 395 (1925)).

Addition to Rubber

I. *Addition to Purified Rubber Hydrocarbon.*—Five grams of rubber hydrocarbon, purified by the standard method of Harries, were dissolved in 200 cc. of chloroform and shaken with 406 cc. of 0.95 per cent aqueous hypochlorous acid (= 1 mol) at 0–5° C. The addition was complete in 20 hours. The lower chloroform layer was removed, filtered, and poured into alcohol to precipitate the additive product; a small amount of gelatinous material floating in the aqueous layer was disregarded. The precipitated reaction product was a soft, rubber-like mass, soluble in benzene, chloroform, and carbon tetrachloride, insoluble in acetone and alcohol. When freed from solvent it was a tough, horn-like, pale brown material which was completely insoluble, though swelling considerably in many organic liquids. It was somewhat unsaturated toward bromine. For analytical purposes the freshly precipitated material was redissolved in benzene, filtered, reprecipitated with methyl alcohol, partly dried *in vacuo*, cut into small pieces, and finally freed from solvent by keeping in a vacuum desiccator over sulfuric acid until its weight remained constant (found: Cl 27.1, C 57.4, H 6.83%; C_5H_9OCl requires Cl 29.4, C 49.9, H 7.48%).

The above addition was repeated using 10 grams of rubber dissolved in 500 cc. of carbon tetrachloride. When addition was complete, the precipitated gelatinous material was removed by straining through a perforated disc; the carbon tetrachloride solution was then filtered and poured into alcohol as before, yielding a tough material similar to that described above (found: Cl 25.1%). The gelatinous material was insoluble and passed on drying into a coarse white powder weighing 4.3 grams (found: Cl 45.1%). On the assumption that this material was a chlorinated chlorohydrin, the chlorine content corresponded to the composition $C_5H_8OCl_2$; on the basis of this formulation 4.3 grams of the material represented 1.9 grams of rubber, and its total chlorine content represented 2.9 grams of hypochlorous acid, leaving 4.7 grams of hypochlorous acid to react with the remaining 8.1 grams of rubber initially taken. The chlorine content of the additive product resulting from these latter proportions of reactants should be 24.8 per cent, and this figure is in close agreement with that found above for the initially soluble chlorinated product (25.1 per cent).

In a further experiment a considerable excess of hypochlorous acid (5 mols) was added to 2 grams of the purified rubber in chloroform solution and kept at 0° C. for three days. A considerable amount of free chlorine and hypochlorous acid still remained at the end of this period. The lower mobile chloroform layer was washed and filtered and a portion of the solvent, together with the residual free chlorine, was removed at the pump; the concentrated residue was poured into alcohol, thus

precipitating a fine white powder. The dry powder was readily soluble in chloroform, benzene, and acetone, but insoluble in carbon tetrachloride [found: Cl 66.0, OH (Zerevitinov) 8.5%; $C_5H_6OCl_7$ requires Cl 63.4%, OH 7.6%, $C_5H_5OCl_5$ requires Cl 68.8%, OH 6.6%].

II. *Addition to Unpurified Rubber.*—Both crepe rubber and masticated rubber were subjected to the action of hypochlorous acid as above. In each case 1 mol of the reagent yielded some precipitated gelatinous insoluble material of high chlorine content, together with soluble material isolated by precipitation with alcohol. These products were much darker in color than those obtained from purified rubber. Excess of the reagent again yielded a white soluble powder.

III. *Addition to Ether-Soluble Rubber.*—Latex, purified by creaming (Pummerer and Pahl, *Ber.*, **60**, 2152 (1927)), was coagulated and the coagulum extracted first with acetone and then (after drying) extracted with ether in the apparatus described by Pummerer, Andriessen, and Gündel (*Ber.*, **61**, 1583 (1928)). Successive portions of ethereal solution of rubber so obtained were treated with different proportions of hypochlorous acid; this series of additions was, however, not very satisfactory, since the ether itself was vigorously attacked by the reagent when the latter was present in considerable concentration. In those additions in which 1, 2, 6, and 10 mols (respectively) of the reagent were used, the reaction products separated as gelatinous masses. The following products were obtained:

(*a*) (Employing 1 mol of reagent): a white hard mass of chlorine content 29.0%.
(*b*) (Employing 2 mols of reagent): a similar mass of chlorine content 39.5%.
(*c*) (Employing 6 mols of reagent): a white spongy material of chlorine content 48.7%.
(*d*) (Employing 10 mols of reagent): a product similar to (*c*) of chlorine content 49%.

In the formation of the last two products most of the reagent reacted with the ether.

IV. *Treatment of the Ether-Sol and Ether-Gel Components of Rubber with Excess of Hypochlorous Acid.*—The sol and gel rubber separated by the above ether extraction (see above) were both freed from ether and then separately extracted with acetone, dried, dissolved in chloroform, and finally submitted to the action of 10 mols of hypochlorous acid for 3 days at 0° C. The products isolated in each case by precipitation with alcohol were fine white powders readily soluble in chloroform, benzene, and acetone. A considerable difference was found in the chlorine contents of the two products; thus for that derived from sol rubber the chlorine content was 53.5 per cent and for that from gel rubber 65.8 per cent.

The authors are indebted to the Rubber Growers' Association, for whom this work was carried out, for permission to publish, and they express their thanks to the Modified Rubbers Research Committee for valuable advice.

[Reprinted from Bulletin of the Rubber Growers' Association, Vol. 15, No. 12, pages 653–666, December, 1933.]

Textile Finishes Research

The following is an Interim Report by H. P. Stevens (Consulting Chemist to the Rubber Growers' Association, Inc.), dealing with an investigation carried out on behalf of the Technical Research and Development of New Uses Committee.

Introductory and Summary

The investigation was initiated with the object of using latex or rubber dispersions as a component of the sizes used for calico printing, dyeing, and stiffening, particularly as regards retention of stiffening ingredients and fillers. Dr. Stevens had, as collaborator, in the investigation, Dr. R. Gaunt, of Manchester, and facilities placed at the disposal of the Association by a firm of Textile Manufacturers. The research assistant who worked under Dr. Gaunt's supervision also availed himself of facilities afforded by the College of Technology, Manchester.

The present report summarizes experimental work carried out by the research assistant, and the following are the more important matters dealt with:

The microscopic examination of latex impregnated threads is of importance in showing that latex merely penetrates between the fibers but does not penetrate the fiber itself, and that modification of the fiber surface such as by mercerization or xanthation does not result in a closer union of fiber and rubber. The basic conditions under which fabrics take up latex have been investigated and it has been shown that the method of "padding" adopted considerably modifies the results. Under some conditions latex serum appears to be preferentially absorbed so that there is a deficiency of rubber in the cloth. The loss of rubber on soaping padded cloths is a mystery which has not been solved.

Much of the work has been devoted to preventing the stickiness or damp feel of latex-treated fabrics. This defect can be eliminated to a great extent by soaking the finished fabric in warm water, but such treatment would not be practicable on a large scale. A satisfactory method of eliminating stickiness has not yet been found. In some cases when tackiness had disappeared the improvement had resulted from the oxidation of the rubber. The cause of the tackiness is not known except that it is probably due to a component in the latex. Attempts to remove this from the latex as by dialysis or the use of centrifuged latex were unsuccessful.

A new material made by impregnating stockinette with latex is of interest. The stretch is greatly reduced, but a strip returns after stretching and maintains a tension when stretched like elastic webbing, though to a much less extent. This product may prove useful for bandaging and similar purposes. Also the use of latex as an adhesive for joining lengths of cloth in finishing processes is under trial. Preliminary work on the treatment of cloth with colored latex has been done.

This mode of producing colored finishes will require further investigation. The full report is as follows.

Preliminary Experiments

As a preliminary experiment latex was incorporated in a standard finishing mixture, which included starch paste, china clay, and olein oil. This mixture was padded on to cloth. A slight tackiness was noticed, which was easily overcome by increasing the amount of china clay in the mixture.

Experiments were then carried out increasing the amount of latex in the mixture,

padding on to cloth and estimating the amount of finish removed by washing. It was found that the amount of filler washed away was approximately twice as much in the case of a latex-free finish as in the latex finish.

Attempts were made to confirm the statement made by E. A. Hauser that complete penetration of threads by latex is not obtained unless wetting agents are used. The scheme employed was roughly that employed by Hauser. The thread, which in this case was cotton, was immersed in latex or latex modified by the addition of a wetting agent, and dried. It was then embedded in paraffin wax and after cooling sufficiently was cut into small blocks. The blocks were then clamped in a vice and a thin slice of the wax containing the thread was cut by means of a razor. The wax was so cut that a cross-section of the thread was obtained in the slice. The section was then mounted on a microscope slide, covered with a cover glass, and the whole immersed in concentrated sulfuric acid. The rubber on the thread is turned a characteristic reddish brown, while the cotton should be destroyed. The preparation was then washed and viewed under the microscope. The reddish brown coloration of the rubber enabled the observer to see how far the rubber particles had penetrated the thread. Unfortunately, on account of the difficulties met with in embedding the thread, in cutting a suitably thin section and in the unsuitability of the embedding material, the results obtained were not everything that could be desired. The materials used for embedding included gelatin, Japan wax, and paraffin wax. The latter was found to be most suitable, especially if cooled well in ice. Many wetting agents were tried. A more careful and detailed investigation of the penetration of latex into cotton threads was subsequently carried out, and will be described later.

A further part of the preliminary work consisted of attempts to obtain a moderately thick deposit of rubber on carding fabric. The best method was found to be that mentioned earlier under the Patent Specification 284,608, that is, the heat sensitization of latex. The carding fabric was secured round the steam heated aluminum tube, which was dipped into the sensitized latex. Vulcanizing ingredients were mixed in the latex, and the rubber could be vulcanized on the tube after the deposition was completed. The bond between the rubber and the fabric was good, and the product was altogether quite satisfactory.

Other methods of obtaining thick deposits of rubber on carding fabrics were tried. Ordinary latex was thickened with 5 per cent aluminum sulfate solution. This was spread on to cloth and dried. A good deposit was obtained, though the bond was not too good and the surface of the rubber was uneven. The surface was improved by spreading a layer of ordinary latex on to the dry rubber. The bond between the rubber and the cloth could be improved by coating the fabric with a mixture of latex and wetting agent and drying down.

In another method the fabric was wrapped round the former and dipped alternately into the latex and 5 per cent acetic acid. Thus the latex was coagulated on the fabric. On drying, the rubber was found to have an uneven surface and the bond between the rubber and the fabric was poor, but could be improved by the method mentioned previously.

In another method 1 per cent acetic acid was added to latex slowly with constant stirring. Enough acid is added to give a compact coagulum when the mixture is heated on a water bath. It was found that 40 cc. of 1 per cent acetic acid added slowly and with constant stirring to 10 cc. of latex was the minimum quantity required to produce a compact coagulum and clear serum after 15 minutes' heating at the temperature of a water bath. Cloth secured on a tube was immersed in the flocculated latex and heated. The coagulum of rubber was formed on the tube. The serum was poured away and the rubber well rolled until a smooth surface was

obtained. On drying, the product was found still to have an uneven surface, though the bond was good.

Impregnation of Cotton Threads with Latex. Microscopic Investigation

The investigation of the impregnation of cotton threads by latex was continued. The ordinary method for cutting sections of threads was found to be unsuitable in some ways for the obtaining of good sections of rubberized threads. The method finally adopted was briefly as follows. Threads were teased out on a piece of ordinary bleached cotton cloth, and soaked in latex. On drying the thread was surrounded by a film of rubber. The rubberized thread was placed in a brass mold and embedded in a mixture of paraffin wax and stearic acid. The block of wax was removed from the mold, cut down to the size requisite for mounting on the fiber blocks, and the excess of wax cut away, leaving a pyramid in the center of which was the latex treated thread standing vertically. The surface of the wax was cooled by immersing in a mixture of ice and salt. The mounted pyramid was transferred to the table of the microtome and thin slices of the wax were cut by means of the sharpened microtome blade. The thickness of the section was 5μ. The section was then transferred to a microscope slide on which was a thin covering of Mayer's albumen. On warming the slide, the cotton thread was fixed vertically by the adherence of the thread to the slide, this being brought about by the albumen. The heat had also melted the paraffin wax. The slide was then washed in xylene, which dissolved the wax, and alcohol, which removed the excess xylene. The sections were then covered with a cover glass and viewed under the microscope. The drawbacks of the method can be easily seen to be the use of xylene, which swells the rubber and so causes indefiniteness in the results. The fibers too had a tendency to fall over on their sides, thus rendering a view of the cross-section impossible. Other solvents for paraffin wax were tried, but each which acted efficiently had the same swelling action on the rubber. Thus it was not advisable to remove the paraffin wax. If the wax was to remain it was necessary to stain the rubber in order to obtain a clear indication of the penetration. Sudan III, a red, fat soluble dyestuff, was found to stain the rubber best. Further, the wax could be rendered more or less invisible by mounting the sections on the slide in some material which had the same refractive index as paraffin wax. Chloral hydrate jelly was found to work best, though in time it dissolved the Sudan III out of the rubber. Eventually glycerol jelly was found to be quite suitable as a mounting material instead of chloral hydrate jelly. It did not dissolve the Sudan III out of the rubber. The whole scheme then used was as follows: The thread was soaked in latex, dried, and stained in a boiling saturated solution of Sudan III in alcohol. After drying the thread was embedded as before in a 50–50 mixture of paraffin wax and stearic acid, cooled, and transferred to a fiber block. A suitably thin section was cut and mounted on a microscope slide in glycerol jelly. The section was then ready for viewing. It could be seen from the slides that the impregnation of bleached threads by latex appears to be much the same as the impregnation obtained by incorporating wetting agents in the latex. The advantage of using wetting agents is seen in the case of gray, *i. e.*, unbleached threads. Treated with latex alone, the thread could be seen with a ring of rubber outside the thread, there being very little penetration of the latex into the thread. Using a wetting agent, complete impregnation was obtained. The natural fats and waxes and the size applied before weaving account for this. It is perhaps necessary to define complete impregnation of the thread. By complete impregnation, in the sense in which it is used above, is meant the penetration of the latex particles into the

center of the thread, but not into each individual fiber. This would seem to be impossible, taking into consideration the size of the latex particles. It is highly improbable that particles of such dimensions could penetrate the cell wall of the cellulose. This seems to be borne out by the experimental work done. The action of wetting agents seems to be confined to a reduction of the surface tension and a diminution of the angle of contact, factors which bring about better penetration. In the case of the latex and bleached cotton, there seems to be no necessity for any rearrangement of these factors influencing penetration. It seems unlikely that the size of the latex particles is altered by addition of wetting agents. Microscopic tests were carried out to investigate this, but no evidence was obtained to refute the above statement. Many wetting agents were used, chief of which were Igepon A.P., Sulphonated Lorol, Gardinol C.A.P.A.S., Nekal B.X., Perminal K.B. Whichever wetting agent was used, the effect was always the same. The threads were impregnated, but each individual fiber was clear cut and showed no sign of containing rubber.

Efforts were then made to obtain penetration of the fibers of the thread with latex. The first attempt was to apply the latex to the thread while the cellulose was in the swollen condition. The swollen cellulose was obtained by immersing the cotton thread in 48 degrees Tw. caustic soda for a short period (30 seconds). The cotton was then washed and immersed in latex, dried, stained, and mounted as described previously. On cutting the sections and viewing them under the microscope, the fibers could be seen swollen but quite free from rubber. The latex had penetrated between each fiber but not into the cellulose structure.

Attempts were then made to obtain superficial xanthation of the cellulose prior to immersing in the latex. It was thought that if the cell wall had been rendered plastic by the xanthating process, the latex particles might possibly find access to the interior of the fibers. The xanthation was carried out by suspending caustic soda treated threads in carbon disulfide vapor till a full yellow color was obtained. The thread was then treated with latex and the same preparation for viewing carried out as described above. It was found that the fibers in places were stuck together, which indicated that the plastic condition had been attained. There was no sign of the rubber entering the fibers. A thread treated with latex *in vacuo* also showed no sign of penetration of the latex into the fibers. Latex was applied to a thread which had been teased out of a piece of heavily calendered cloth. On cutting a section and viewing under the microscope, the latex seemed to have penetrated quite easily between the fibers.

Thus it appears quite simple to impregnate threads with latex without the use of a wetting agent. On the other hand it does not seem possible to obtain impregnation of the fibers with latex.

The penetration of threads with rubber solutions was investigated. A 10 per cent solution of rubber in benzene was used. Threads were soaked in the solution, dried, stained, and sections cut in the same way. It was found that the penetration was only as good as that given by latex, provided the threads were left in the solution for a sufficiently long time. This is probably due to the higher viscosity of the rubber solutions. Again there was no penetration into the cellulose. Gray threads were more easily penetrated than bleached threads. Diluted latex (10 per cent) was found to give very similar results to ordinary latex.

Later photomicrographs were made of a typical section of mercerized cotton thread treated with latex. The rubber, showing black on the photograph, is seen to surround the individual fibers of the thread, while the fibers themselves are seen white. The lumens of the fibers should not be mistaken for rubber. It is unfortunate that the red-stained rubber should show black on the photograph in

the same way as the lumen, which appeared dark before photographing. (See Fig. 1.)

Latex Applied to Cloth

Latex was applied to cloth with the intention of obtaining a showerproof fabric. Latex of various concentrations was padded on to the cloth from a pair of rollers, the bottom one of which was furnished with latex. As the concentration of latex increased (10 per cent to 40 per cent) the amount of rubber on the fabric increased also. The samples were not, however, sufficiently waterproof to give a good shower-

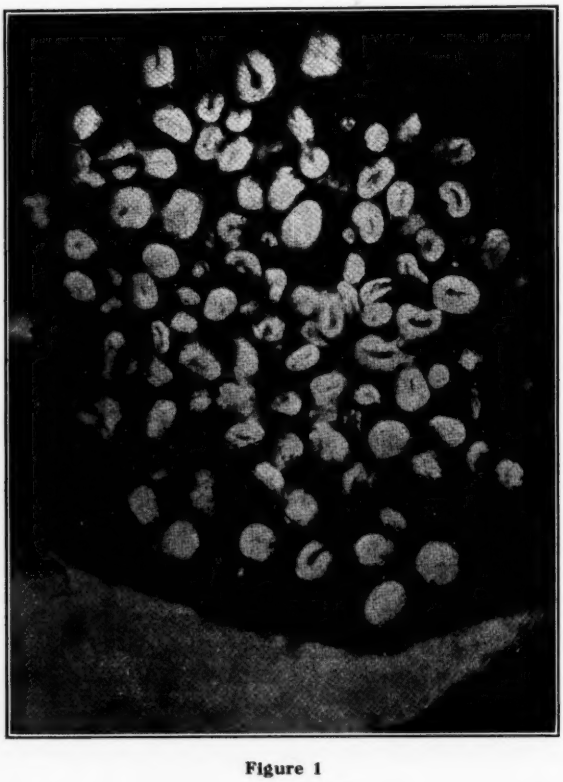

Figure 1

proof fabric. Cloths were then padded repeatedly in 40 per cent latex. They were dried after each pad. After the third pad tackiness became evident. With each successive pad there was an increase of approximately 3 per cent rubber on the cloth. Samples with a high percentage of rubber were not sufficiently waterproof to merit the use of latex as a waterproofing agent. The non-waterproof character of the samples is no doubt due to the fact that rubber is not water repellent in the same way as wax. The tackiness of samples, which increased with each successive pad, after the third pad, was a distinct drawback. The cause of the tackiness seems to be the water-soluble substances of the latex, which are absorbed when the latex is dried. Small quantities of many substances were added

to the latex to try to prevent the tackiness. The substances included Nonox S, emulsified linseed oil, emulsified tornesite in benzene, *p*-nitrophenol, stearic acid, and paraffin wax emulsion. Wax emulsions if added in large enough quantities to the latex prevented the tackiness. The other substances had little effect. If a 30 per cent solution of tornesite in benzene were spread on to a tacky sample and dried, the tackiness was overcome. The product was also showerproof, but airproof as well, which it is desirable to avoid if possible.

Determination of Water Absorption of Latex Treated Cloth

A comparative method for estimating the amount of water absorbed by samples treated with latex was evolved. Samples were prepared which had received one, two, three, four, and five treatments with latex. Thus samples were obtained with increasing amounts of rubber on them. They were conditioned in a desiccator over concentrated sulfuric acid. After leaving overnight in the desiccator they were weighed in a stoppered bottle. They were then soaked in water, squeezed off through a mangle, placed immediately in a stoppered bottle, and reweighed. Thus the amount of water absorbed by the fabric was estimated. This was expressed as a percentage of the original weight. It may be seen from the following table how the water absorption varies with the percentage of rubber on the samples:

No. of Pads	Percentage Rubber	Percentage Water Absorption
Control	..	115
1	20	55
2	22.5	41
3	25	37
4	28	33.5
5	31	33.5

Boiling Out Treatment

Experiments were tried to remove the tackiness from the samples padded many times in latex, by soaking them in hot water for a considerable time. After five hours' treatment with hot water and allowing to stand overnight, the tackiness was completely removed from a sample which had been padded three times in ordinary latex. Samples were then prepared on which there was a high percentage of rubber. They were soaked in hot water by day and cold water overnight, the hot water being changed each hour. After continuing this treatment for 72 hours, the tackiness was removed. The operation was carried out in large beakers placed in a large water bath which was kept boiling. The samples became slimy during the boiling out and picked up dirt. After the tackiness was removed they were easily cleaned by a hot soap solution treatment.

Tests were carried out on the samples which are tabulated below:

	Per Cent
Original per cent rubber	34
Per cent water absorption	9
Per cent water absorption after removal of tackiness	13
Per cent removed by boiling	5
Further per cent removed by soaping	17

Thus it is seen that after removing the tackiness the water absorption is increased. Further, a very large percentage of the rubber is removed by the hot soap washing. On other samples the soaping was prolonged and the cloth was rendered slimy, with a large decrease in weight on the original. Thus it would appear that the rubber was emulsified by the hot soap. It was thought that

vulcanization might reduce the tackiness, and if not, prevent the formation of the slimy substances during the hot soaping. Vulcanizable latex was made up according to the following:

Latex	250 cc.
Colloidal zinc oxide (50 per cent)	5 g.
Colloidal sulfur (50 per cent)	2 g.
Sodium diethyldithiocarbamate	1 g.

The mixture was padded three times onto the cloth and heated at 60° C. for 16 hours. There was no diminution of the tackiness but when the samples were boiled in water or in soap, the slimy product was not formed. Soaping, however, does not prove so effective in removing the tackiness as water. More detailed experiments on the vulcanization of latex will be described later.

The Use of 60 Per Cent Latex

Paddings of 60 per cent latex were carried out on cloth. It was expected that since the tackiness was caused by the serum substances, the tackiness would be diminished using 60 per cent latex from which the serum substances are largely removed. This was found not to be the case. Tackiness was still evident when samples had been padded twice with 60 per cent latex.

Investigation of Selective Absorption

It had been noted previously that when cloth was padded with latex and dried, the percentage of rubber on the cloth was about 20. When the cloth was padded with water alone, the increase was over 100 per cent. Therefore with the concentration of latex nearly 40 per cent there ought to be about this percentage increase in weight when the cloth is dried. A piece of cloth was dipped in ordinary latex, squeezed off and weighed wet. The increase in weight was 90 per cent. On drying the increase in weight was 30 per cent, which represented the dry rubber on the cloth. This sample was not tacky, though when a sample was obtained which contained 30 per cent rubber applied by squeezing through rollers, the bottom one of which was furnished with latex, it was tacky. Thus, it would appear that there is selective absorption by the cotton when the latex is applied from the bottom roller of a pair. The water-soluble substances seem to be absorbed in preference to the rubber particles. This would explain the tackiness and also the low percentage increase in dry weight, after padding. When the cloth is dipped and then squeezed, no tackiness is apparent, though the increase in weight is 30 per cent. The rubber particles and water-soluble substances seem to have equal chances of being absorbed when the latex is applied in this way.

Sixty per cent latex was applied by the method of dipping and squeezing (padding). After one pad the increase in weight was 43 per cent, after two pads, 60 per cent, when a slight tackiness became evident, and after three pads the increase in weight was 75 per cent, the sample being very tacky.

Dyeing Experiments

Samples were prepared containing increasing amounts of rubber, the latex being applied by the method of squeezing between two rollers, the bottom of which was furnished. More samples were prepared by the dipping and squeezing method. These samples were dyed along with a control (ordinary cotton) in a 1 per cent dyeing of Chlorazol Sky Blue G.W.S. for one hour at the temperature of a boiling water bath. As the percentage rubber increased by the first method of padding, the shade of the resulting sample grew lighter. As the percentage rubber in-

creased by the second method of padding, the shade became deeper than the control. Thus is seems that the water-soluble constituents of the latex resisted the dyeing. Why the dyeing should show a deepening of shade on the samples which had been treated with latex by the dipping and squeezing method is not known, unless the rubber itself absorbs some of the dyestuff.

Dialysis of Latex

The cause of the tackiness of samples padded repeatedly with latex had been deduced as due to the water-soluble components of the liquid serum. They appear to be absorbed by the rubber when the latex is dried down. Such objectionable components may be removed by the prolonged heating of the samples in water, thus allowing a slow diffusion of the substances from the rubber to the water. This process would cause great inconvenience on a works scale. An attempt was therefore made to free the latex of the undesirable components before its application to the cloth. This was carried out by an arrangement for dialyzing the latex. The accompanying diagramatic sketch shows a porous pot, through

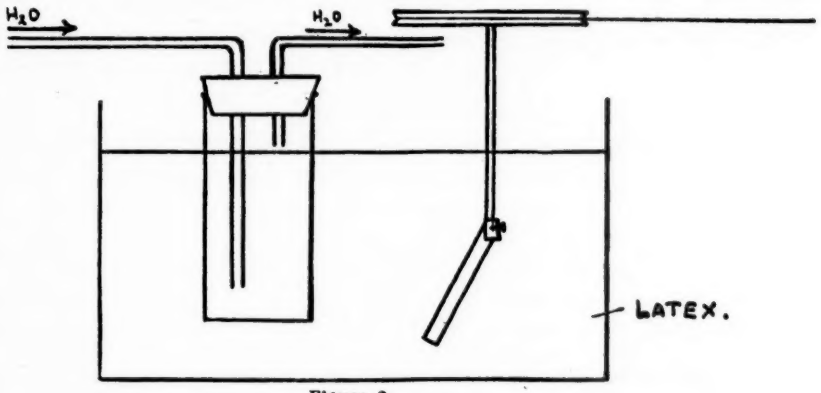

Figure 2

which is passing a continuous stream of water, immersed in latex contained in a large glass tank. (See Fig. 2.) In order to prevent clogging of the pores of the pot by the latex particles, a stirrer was arranged to keep the latex in motion. The stirring was effected by means of a rotating rectangular glass plate held obliquely by the clamp. Thus, the latex is kept swirling round the porous pot.

In theory the water-soluble (crystalloid) components should diffuse through the pot and be carried away by the stream of water. Further, the ammonia should diffuse in the same way. Thus, the p_H of the latex should diminish as the process proceeds. This was found to be the case. The p_H value of the latex was tested periodically by means of the B.D.H. Universal Indicator. More ammonia was added after each day's run to bring the p_H up to the original value. This diminishing of the p_H may be also due to evaporation of the ammonia. As the experiment proceeded the latex assumed a creamy color. This was found to be due to impurities in the latex. Before the experiment commenced, the latex was noticed to have a grayish green sediment which if separated off gradually became brown when exposed to air. The browning of the latex may be explained by oxidation of this impurity. Attempts were made to filter off this impurity, but the latex would not pass through the filter paper, even on application of a vacuum. Apparently,

the pores of the paper became clogged before any appreciable amount of latex passed through. Various thicknesses of cloth were tried, by which an amount of the impurity was removed. A further quantity was removed by allowing the latex to stand over the week-end in tap funnels and separating off. Even then the latex was creamy owing to the fine suspension of the impurity. The experiment was kept running continuously for 24 hours. Cloths were padded after 6 hours, 13 hours, and 24 hours without any apparent diminution of the tackiness after padding three times. Vulcanizing ingredients were incorporated in the dialyzed latex, and the mix padded three times onto cloth. When the sample was heated on a hot cylinder after half an hour, black spots covered the cloth. These were apparently due to sulfide formation during the heating. When treated with dilute acid hydrogen sulfide was evolved. When the samples were heated for a longer time at a much lower temperature, 60° C., no black marks appeared. The products, however, still showed tackiness. Fresh latex was drawn from the iron containers and allowed to stand for a few days in Winchester bottles. The latex was decanted and placed in the container surrounding the porous pot. The

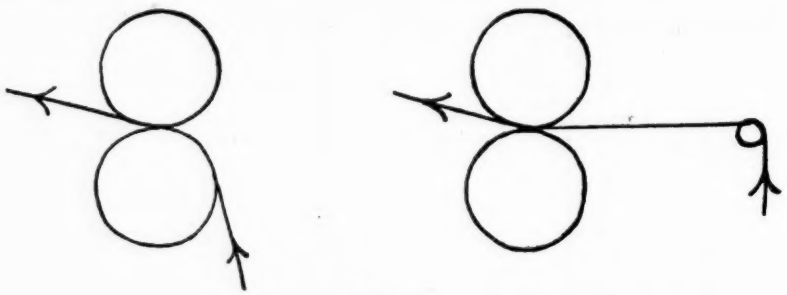

Figure 3

particles of iron or an iron compound seemed to have been eliminated, for the latex remained pure white throughout the experiment. There seemed to be no diffusion of the serum substances through the pot, for on padding such latex after 12 hours on to cloth, the results were just the same as when ordinary latex was padded onto the cloth. The experiment was therefore abandoned.

The Application of Latex to Stockinette

Stockinette material (knitted wool) was treated with latex in the same way as cotton cloth, *i. e.*, a weighed sample was dipped in latex and squeezed through the mangle. After drying an increase in weight was obtained, which was the percentage of rubber on the fabric. It was found that this percentage was 15.4. After the samples had received six pads, the increase in weight was 64 per cent. It was noticed that the stretch of the fabric was considerably diminished as the rubber increased on the fabric. It seemed possible, however, that by virtue of its rubber content, the fabric would have a more permanent, if less, elasticity. The water absorption of the fabric before application of the rubber was 40 per cent. Rubberized, *i. e.*, having had six pads with 40 per cent latex, the stockinette absorbed 13 per cent water. A rather undesirable feature of the results was the fact that the strips of stockinette increased considerably in length during the repeated squeezing and drying. It was thought that this might be due to the drying between each pad, but unless drying took place there was only an increase in weight of 13 per

cent after six paddings. The length too seemed to have increased just the same during the process. The other factor, squeezing, might have had some influence on the length of the strips. The diagram will illustrate the two methods of squeezing. (See Fig. 3.)

Method 1 was the method used when a large increase in length was observed. The strip is pulled up by the squeezing rollers. Thus the strip may be under tension when it is squeezed. This possibly accounts for the increase in length. Method 2 was the method adopted for tensionless squeezing. The strip is passed over a guide roller which is on a higher level than the rollers. Thus there is no tension on the strip when it passes between the rollers. The increase in length of the strips padded in this way was less than that obtained by method 1.

The products were quite good, though tackiness was noticed. Vulcanizable latex was used. It was made up as follows:

Latex	250 cc.
Finely powdered sulfur	2 g.
Zinc oxide (50 per cent)	10 g.
Sodium diethyldithiocarbamate	1 g.

After padding six times in this mixture and drying between each pad, the wool was heated for one hour on a steam-heated cylinder. The fabric before heating was a light brown shade. After the heating it was unevenly colored dirty gray. This was possibly due to sulfide formation mentioned previously. The rubber seemed to be well vulcanized and was not tacky. Elasticity of the fabric was very small. The product might possibly be of use as a surgical support.

Vulcanizable Latex Paddings

Experiments have been mentioned previously in which vulcanizable latex has been used to get rid of the tackiness of latex-treated samples. The tackiness did not seem in any way diminished. It has been noticed in the case of the stockinette experiments that the tackiness is overcome by using vulcanizable latex. This mixture was again tried on cotton cloth. It was padded three times, *i. e.*, until tackiness was evident. During the heating process on the hot steam-heated cylinder, blackening was noticed. After half an hour the tackiness was overcome and the cloth had quite a good feel. It was thought that the blackening might be due to excess of the vulcanizing agents. The mix then used was as follows:

Latex	250 cc.
Zinc oxide (50 per cent)	2 g.
Sulfur	2 g.
Sodium diethyldithiocarbamate	1 g.

When such a mixture is padded on to the cloth and heated, the sample becomes non-tacky, though black specks appear on the cloth. It was supposed that vulcanization of the rubber had taken place. The blackening was found to be due to sulfide formation since the cloth, if boiled in dilute acid, gave off hydrogen sulfide. In order to determine the cause of this sulfide formation, experiments were carried out on each of the components of the vulcanizing mix. Samples were padded in suspensions of the various ingredients without the latex:

1. 1 per cent sodium diethyldithiocarbamate in water
2. 1 per cent sodium diethyldithiocarbamate in water
2 per cent zinc oxide in water
3. 1 per cent sodium diethyldithiocarbamate in water
2 per cent zinc oxide in water
2 per cent sulfur in water

The samples were dried and heated at 100° C. None showed blackening. Each of the ingredients was then mixed with latex and padded onto cloth.

4. { 1 per cent sodium diethyldithiocarbamate
   { 250 cc. latex
5. { 2 g. zinc oxide
   { 250 cc. latex
6. { 2 g. sulfur
   { 250 cc. latex

Numbers 4 and 5 showed no blackening, 6 showed blackening on heating at 100° C. The blackening must therefore be due to a reaction between the sulfur and latex. Or the sulfur may be impure. The blackening still took place if the sulfur was diminished to 0.5 g. on 250 cc. latex. Vulcanizable latex was then heated at 100° C. A black sediment settled at the bottom of the container. The latex was decanted off and the sediment washed and filtered. It was found to be iron sulfide. It was soluble in dilute acids, with evolution of hydrogen sulfide. On adding potassium thiocyanate to the solution a red coloration was given. This proved that the black substance was iron sulfide. A sample of sulfur used in the mix was burnt. A black deposit was obtained which proved to be ferric sulfide. The blackening then is due to iron impurity in the sulfur, which combines with the sulfur during the heating process. A fresh sample of sulfur was obtained which contained very little iron. This was used in the mix and the samples after heating at 240° F. for 15 minutes showed no blackening and were non-tacky.

Miscellaneous Work

The work already described has been the main course followed. In addition to this other work has been done, which being of a disconnected character is grouped under this heading of miscellaneous work.

Latex was used as a substitute for sewing two ends of cloth together. It was found to work excellently, if the join was ironed. A very good bond was produced. Thus latex may quite possibly find application in textile processing where sewing is a definite disadvantage.

Latex was also used to give a suitable resilient backing for typewriter ribbon which is intended to displace carbon sheets for producing carbon copies. A viscous solution was necessary for spreading. This was obtained by mixing latex and 20 per cent casein solution in equal proportions and spreading onto the ribbon. A good resilient film was obtained. The spreading was done by means of a knife fastened to the bench. The mixture was placed at one end of a strip of cloth and the cloth passed under the knife. Thus a miniature spreading machine was obtained.

Rubberized Cloth and Linseed Oil

Cotton treated with linseed oil, then heated to bring about oxidation of the oil, is used as an electrical insulating material. Its defect is that the cotton is tendered by the oxidized oil. It was thought that if the cotton were first treated with latex and then linseed oil, a better insulating material would be obtained, in which possibly the cotton would not be tendered by the oil, and so give a stronger product. Samples were prepared in which the cotton threads were completely covered with rubber, *i. e.*, the samples were padded with latex until they became tacky. Double boiled linseed oil was then spread on to samples which were then heated at 110° C. until a full yellow color was obtained. The product did not seem to possess any properties of outstanding merit over the cotton and oxidized oil product.

Dipping Experiments

Cloths were dipped in latex and allowed to dry without squeezing. Cloth with a high percentage of rubber is thus obtained. Using ordinary latex the product was tacky, which in some respects was a drawback to its use. If vulcanizable latex were applied in the same way and the product heated, a non-tacky product resulted. A better product is obtained if the sample is dipped twice in vulcanizable latex, drying it between each dip. A sheet of rubber is then obtained which seems to retain a slight tackiness even after a strong vulcanizing at 240° F. This may be masked by dusting the rubber lightly with French chalk. The product could be used for aprons or tablecloths, now on the market made of rubber entirely. Their drawback is that they may easily be torn. Sheets of rubber backed by even poor quality cloth would be far stronger than these products.

Influence of Time on Absorption of Latex

Weighed conditioned samples of cloth were dipped in latex and squeezed immediately. They were left to dry and then weighed after conditioning. Other samples were dipped in latex, allowed to stand for five minutes, then squeezed off, dried, and weighed. In each case there was an increase in weight of 33 per cent, thus showing that the time of immersion in latex does not influence the amount of rubber on the sample.

Colored Latex

Proprietary colors prepared for latex work as aqueous dispersions were easily compounded with latex. The mixture was padded onto cloth, but uneven shades were obtained from some colors, owing to the comparatively low degree of dispersion of the colors. All the shades lacked brightness, and so were only partially satisfactory.

Latex and China Clay

As a preliminary to the work of incorporating fillers in latex intended for application to cloth, china clay was mixed with latex (a little casein was used as protective colloid) and the resulting mixture padded on cloth.

Latex	100 cc.
China clay	80 g.
10 per cent casein	5 cc.

The finish obtained was good, and was considerably improved by ironing, giving the cloth a smooth handle.

A curious property of latex-treated cloth was also noticed. If cloths which had been padded in latex till they were tacky were then padded in water and hung to dry, after a month's exposure to the air, the tackiness disappears and the samples have quite a stiff handle. A suitable explanation of this has not been found, but it is thought that it may be due to superficial oxidation of the rubber.

NOTE.—This supposition has since been proved to be correct, as the rubber was found to have resinified.

[Reprinted from Bureau of Standards Journal of Research, Vol. 11, No. RP585, August, 1933.]

Effect of Temperature and Frequency on the Dielectric Constant, Power Factor, and Conductivity of Compounds of Purified Rubber and Sulfur

A. H. Scott, A. T. McPherson, and Harvey L. Curtis

I. INTRODUCTION

The authors have previously reported results[1] on the electrical properties of a series of rubber-sulfur compounds which were made from commercial rubber and were measured at 25° C. with 1000∼. The present paper reports results on the electrical properties of a similar series of compounds made from purified rubber and measured over a wide range of temperature and frequency. Sufficient data have been obtained to enable one to determine the dielectric constant and power factor for any composition of rubber and sulfur at any useful temperature and at any normal frequency.

The results obtained in this paper do not entirely confirm the conclusions of the previous paper. When the electrical measurements reported in that paper were plotted as functions of the per cent of combined sulfur, curves were obtained which showed changes in direction at compositions corresponding to simple, empirical formulas. From this evidence as well as from a consideration of changes in density with composition, it was inferred that "the existence of a definite compound of empirical formula $(C_5H_8)_2S$ is indicated by all the properties which have been studied. Evidence for the other three compounds $(C_5H_8)_4S$, $(C_5H_8)_3S$, and $(C_5H_8)_4S_3$ is less complete."

Soon after that paper was published, it was pointed out by Kimura, Aizawa, and Takeuchi[2] that the electrical properties are functions of the temperature, and by Kitchin[3] that they are functions of the frequency at which measurements are made. Kimura and Namikawa[4] pointed out that the density and coefficient of expansion of the rubber-sulfur compounds likewise vary with the temperature. Hence the positions of the maxima and minima which were observed in the earlier paper, and were attributed to the formation of definite compounds of rubber and sulfur bear no relation to the chemical structure of the vulcanized rubber.

The present paper is primarily concerned with the description of methods of experimental measurement of the electrical properties and the presentation of the results. A consideration of the results in the light of modern dielectric theory will form the subject of a separate paper.

II. PREPARATION OF SPECIMENS

The specimens were prepared by molding and vulcanizing thin sheets of different rubber-sulfur compounds between aluminum plates, which later served as electrodes. The process of preparation consisted in purifying the rubber, mixing it with sulfur, molding it between prepared electrodes, and vulcanizing the specimen thus formed in an atmosphere of inert gas.

1. Purification of Rubber

The purification of rubber consisted in the digestion of crude rubber or latex with water at about 180° C., followed by washing with water, extraction with alcohol, and drying in an atmosphere of inert gas. The digestion hydrolyzed the proteins, while the washing and extraction served to remove the protein-hydrolysis products, the resins, the sugars, and part of the inorganic salts. The product thus obtained contained about 99.5 per cent of rubber hydrocarbon. The principal impurities were inorganic salts, as indicated by ash, and residual quantities of resins and protein-hydrolysis products, as indicated by a few hundredths per cent of oxygen and nitrogen. This method of purification afforded a simple and convenient method for making rubber hydrocarbon of reasonably high purity in lots of several kilograms. A detailed description of the method of purification and a discussion of the properties of the purified rubber is given elsewhere.[5]

2. Mixing of Rubber and Sulfur

The purified rubber was usually mixed with sulfur in an internal mixer in an atmosphere of nitrogen or carbon dioxide, but some batches were mixed carefully on a roll-mill in air. The rubber and the sulfur were weighed separately, and the batch was weighed after mixing. The weight of the batch seldom differed from the sum of the weights of the components by more than 1 part in 1000. Any

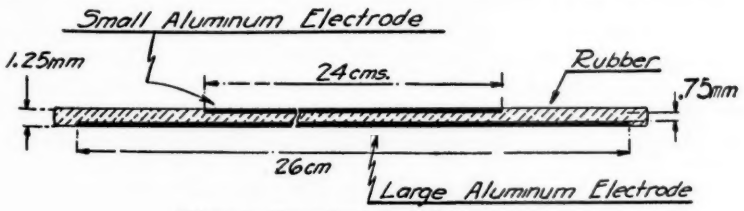

Figure 1—Cross Section of Molded Specimen

greater difference was due to a loss of sulfur by dusting, and the requisite quantity of sulfur was added to correct this loss. The batches after mixing were stored in an atmosphere of inert gas until used for making specimens

The sulfur employed was a commercial grade of ground, rhombic sulfur, specially prepared for use in rubber manufacture. Analysis indicated no impurities except a trace of ash.

3. Electrodes

The electrodes were circular discs cut from aluminum sheet, and were approximately 0.025 cm. thick. They were used in pairs of 24 and 26 cm. diameter, respectively, as indicated in Fig. 1. The electrodes were of two types—one type was made from ordinary polished aluminum sheet, and the other from aluminum sheet perforated with fine holes. The perforated aluminum sheet used for this purpose had 97 perforations per square centimeter; each perforation was of about 0.05 cm. diameter, and was separated from adjacent perforations by about the same distance.

The electrodes of polished sheets were employed in measurements at 25° C. These ordinary electrodes were not satisfactory, however, for specimens that were to be measured over a range of temperature, because differences in thermal expansion frequently caused separation of the rubber and metal. For this reason,

specimens that were to be employed in determining the effect of temperature were made with electrodes of perforated aluminum. Since the rubber was molded into the perforations, excellent attachment to the electrodes was secured at all times.

4. Molding of Specimens

The electrical test specimens were made by placing the requisite quantity of the unvulcanized rubber-sulfur stock in the form of a sheet about 1 cm. thick between a pair of electrodes and pressing it out in a hydraulic press to form a sheet about 0.075 cm. thick between the electrodes. The exact thickness was controlled by the use of a large spacing ring between the platens of the press. Enough of the rubber-sulfur stock was used to permit considerable overflow beyond the edge of the electrodes. The overflow carried most of the entrapped air with it, and thus minimized the quantity of air enclosed in the specimen. A large sheet of aluminum foil was placed on each side of the specimen in order to prevent the overflow from sticking to the platens of the press. The foil was left on the specimen during vulcanization, and up to the time the electrical measurements were made, in order to protect the rubber from oxidation and contamination.

Care was exercised to secure a uniform thickness that could be measured with the accuracy requisite for the determination of the dielectric constant. The platens of the press were plane to within 0.01 cm. over the entire bearing surfaces. The molding was done at about 100° C., and the specimen was left between the platens of the press for 10 minutes in order to permit the rubber to flow as much as it would. The best specimens that were obtained were uniform in thickness to within 2 per cent of the thickness of the rubber, or about 15 μ, over their entire area, but in some cases the thickness of the specimens varied by as much as 5 or 10 per cent. These large variations were traced to inequalities or irregularities in the platens, and could be eliminated by regrinding, which was done whenever they were discovered.

5. Vulcanization of Specimens

After molding, the specimens were vulcanized in an autoclave. Those made during the early part of the investigation were vulcanized in open steam, but the majority of the specimens were vulcanized under pressure in an autoclave filled with carbon dioxide, hydrogen, or nitrogen. An autoclave for this purpose was improvised from a standard 12-inch iron pipe cap, on which a rigid iron plate was bolted as a cover. A gasket made from a ring of wire solder effectively prevented the leakage of gas.

The time of vulcanization in the gas-filled autoclave was between 25 and 40 hours at 140° C., with the gas pressure at 50 or 60 lbs. per sq. in. in excess of the pressure of the atmosphere. Vulcanization in steam was conducted for about 15 hours at 149° C. This relatively long time of vulcanization was intended to bring practically all the sulfur into combination with the rubber. Analysis indicated that this purpose was accomplished in the case of all specimens except those containing the maximum amount of sulfur. Specimens compounded with 32 per cent of sulfur were found to contain 0.5 to 0.8 per cent of sulfur in the uncombined state. Those compounded with 28 per cent of sulfur contained 0.1 to 0.2 per cent of free sulfur, while the specimens of lower sulfur content contained not more than 0.1 per cent of the element in the uncombined state.

III. MEASUREMENT OF THE DIMENSIONS OF SPECIMENS

The dielectric constant and the conductivity of the material of a flat specimen with ordinary electrodes can be computed from the results of electrical measure-

ments, the thickness between the electrodes, and the area of the smaller electrode.

That, however, cannot be done for specimens having perforated electrodes. Here the electrical properties may be arrived at indirectly by determining experimentally a shape factor for each specimen—a procedure which amounts to finding the dimensions of a parallel-plate capacitor which would be equivalent to the specimen under consideration.

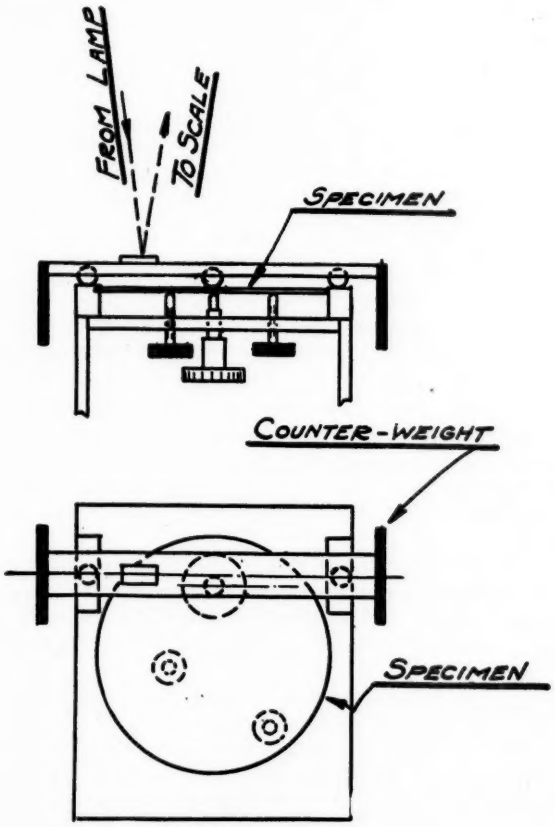

Figure 2—Bar Gage

The bar rotates on the spherical surfaces at each end of the bar. The scale is at right angles to the axis of the bar and the tilting of the bar moves the spot of light along the scale. The micrometer head is provided so that the approximate thickness of the specimen can be set on it and only the variations in thickness need be measured by the bar. The optical lever system is so adjusted that the gage reads in microns.

1. Measurement of Thickness

The majority of the measurements of thickness were made with the dial gage which was used by the authors in previous investigations.[6] This gage, however, was found to be unsuitable because the pressure exerted by the plunger, which had a very small foot, reduced the thickness of the rubber of the softer specimens even through the thin aluminum electrodes. The error from this source was as much

as 2 per cent for some soft rubber specimens, but was negligible in the case of hard rubber. A correction for each composition was determined, and was applied to the measurements which had been made with the dial gage.

Accurate measurements of thickness were made by means of a gage which operates with a relatively slight contact pressure. This gage is a modification of one devised by Dye and described by Rolt.[7] As is shown diagrammatically in Fig. 2 it consists of a steel bar supported on three hemispherical surfaces, the ones at the ends resting on hardened steel supports which are lapped optically flat, and the one at the center resting on the end of a micrometer head. The hemispherical surface at the center is 1 mm. off the line of centers of the other two; thus any vertical displacement of this spherical surface tilts the bar. The optical lever system from the top of the bar is so adjusted that the vertical displacement can be read directly in microns. The micrometer head is provided so that the approximate thickness of the specimen can be set on it, and the optical lever system need only take care of the variations in thickness of the specimen. The bar is so balanced that the pressure of the specimen is small and the compression is negligible for purposes of the present investigation. This was established by comparing the volume of rubber in a specimen as found by dimensional measurements with the volume indicated by the method of hydrostatic weighings. The two methods gave the same volume, within experimental error, whereas if there had been any appreciable compression the volume computed from the dimensional measurements would have been the smaller.

The thickness of each specimen was measured at 19 points, which were so distributed as to represent equal areas. A pattern was employed as a convenient means for locating the points. To test the reproducibility of the average so obtained, several specimens were measured repeatedly with the pattern shifted each time to a new position. The largest variation found in the average thickness was about 1 per cent.

The thickness of the rubber in a specimen was found by subtracting the average thickness of the aluminum electrodes from the over-all thickness of the specimen. This was done mechanically by offsetting the zero of the measuring instrument by an amount equal to the thickness of the aluminum plates of the particular specimen under observation.

The thickness of the aluminum plates was ascertained either by the use of the optical gage described above or by weighing them, measuring their diameters and computing the thickness from these data and the known specific gravity of the aluminum. Measurements on aluminum plates at different points indicated that they were sufficiently uniform to justify the use of the simple average thickness.

2. Measurement of Area

The area of the specimen used in the computation of the dielectric constant and conductivity was obtained by correcting the area of the smaller electrode for the fringe or edge effect. This correction was included in the equations used to compute these electrical properties, and is discussed in a subsequent section of this paper.

The area of the smaller electrode was computed from the average diameter, as determined by measurements with a steel scale in different directions. The diameters of a given electrode seldom varied by more than 0.5 mm., and the accuracy with which the area was determined was about 0.5 per cent.

3. Change in Dimensions with Temperature

The change in area of the electrical test specimen due to thermal expansion was small, and therefore no correction was applied. Taking the coefficient of expan-

sion of aluminum as 23×10^{-6} per ° C., the change in area would be about 1 per cent for a temperature change of 210° C., which is the largest difference between the temperature of dimensional measurement and the temperature of electrical measurement reported in this investigation. In the majority of measurements the change was considerably less than 1 per cent.

The change in thickness with temperature was however of significant magnitude, not only because the coefficient of expansion of rubber is much greater than that of aluminum, but also because the rubber held in a thin sheet between the aluminum plates is free to move in only one direction, so that any contraction or expansion is manifest almost wholly as a change in thickness, the lateral dimensions changing only as much as the aluminum.

To investigate experimentally the change in thickness with temperature, the thickness gage described above was mounted in an electric oven, and measurements were made on representative samples at several temperatures from 25° to 150° C. The results were found to be in accord with those computed or extrapolated from the volume coefficients of expansion reported by Kimura and Namikawa,[8] so these latter coefficients were used as a basis for correcting all determinations for change in thickness with temperature. These corrections amounted in extreme cases to as much as 13 per cent.

IV. MOUNTING OF SPECIMENS FOR ELECTRICAL MEASUREMENT

The specimens were assembled for the electrical measurements in a measuring chamber which was provided with a means for connecting to the specimens. Two different measuring chambers were employed, one being used solely at 25° C. and the other at temperatures below or above 25° C. Several different methods were used for securing and controlling the temperature, but the same method of assembling the specimens and making electrical connections was employed throughout the work.

1. Electrical Connections to Test Specimens

The test specimens were assembled by pairs into test units, two specimens of the same composition being placed with their smaller electrodes together. Electrical connection was made to the smaller electrodes by placing between them an aluminum disc, which was provided with a slender projection that extended from between the specimens. Connection was made to the larger electrodes by pressing against them aluminum discs having projections which extended beyond the edges of the specimens. When the larger electrodes were maintained at earth potential and the smaller, inner electrodes at an elevated potential, the test unit constituted a shielded condenser. In practice as many as 10 of these test units were placed one on top of another in the constant temperature chamber at one time. The smaller electrodes were connected to well insulated, individual measuring leads. The larger electrodes were connected to a common lead. In Fig. 3 a stack of test units assembled for electrical measurements is shown outside the measuring chamber.

To insure good electrical contact between the electrodes and the aluminum discs that were used to establish connections to the leads, brass filings were sprinkled on the surfaces, and a weight of about 7 kg. was placed on the assembly of specimens. Measurements indicated that this reduced the contact resistance to less than 0.005 ohm. Contact resistances at other connections were reduced by sandpapering or scraping the metal surfaces. The weight placed on the top of the specimens was assumed to have no appreciable effect on the thickness of the specimens, since application of the weight did not change the capacitance as measured with 1000~.

2. Chamber for Measurements at 25° C.

The chamber in which measurements were made at 25° C. was a large earthenware jar mounted in a thermostatically controlled oil bath. The test units were

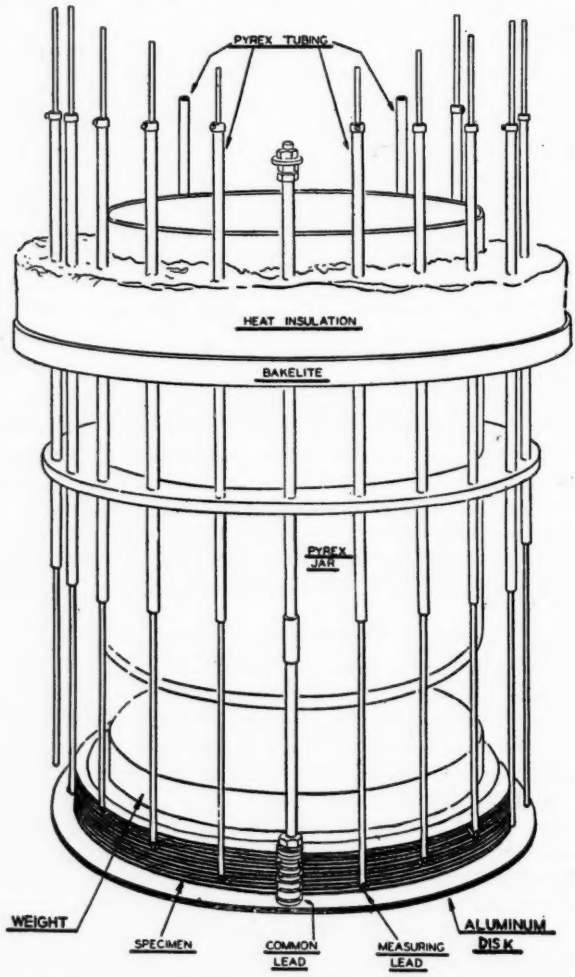

Figure 3—Specimens Mounted for Electrical Measurement at Temperatures from −75° to 235° C.

The specimens are mounted on the aluminum disk suspended from the bakelite cover of the constant temperature chamber (not shown). Measurements are made after the temperature and humidity become constant. The specimens are connected to the bridge by the vertical brass rods. For temperatures below 25° C. part of the cooling liquid is put in the jar mounted in the cover; this produces circulation of the gas in the chamber. When temperatures above 25° C. are used, this jar is filled with a thermal insulating material.

placed on a hard rubber disc which was suspended from a hard rubber cover, the cover being seated on a ledge inside the jar. Electrical connections to the specimens were established by means of brass rods passing through the cover. These

were insulated by paraffin bushings. The humidity was kept low in the chamber by means of a large tray of anhydrous, granular calcium chloride at the bottom. Circulation of the air in the chamber by means of a fan assured uniformly low humidity as well as constant temperature throughout. A further description of this constant temperature chamber, together with an illustration showing the mounting of the specimens in it, and the method of obtaining the lead capacitance, has been given in a previous publication.[9]

3. Chamber for Measurements at −75° to 235° C.

The chamber in which measurements were made over a wide range of temperature was a Pyrex glass jar of about 30 cm. diameter mounted in a constant temperature bath. The test units were mounted on an aluminum disc suspended from a bakelite cover which rested on the top of the jar. The cover with some test units mounted on the suspended aluminum disc is shown in Fig. 3. As is shown, a portion of the center of the cover was cut out, and a smaller Pyrex jar was suspended in this opening so that the bottom of this jar was about 5 cm. above the specimens, and the top extended above the cover. This provided a means for stirring the air in the chamber at temperatures below room temperature, since a part of the cooling liquid used in the bath could be put in the smaller jar, thereby producing convection currents. Pyrex glass tubes were inserted in the cover for the lead rods to pass through in order to furnish better electrical insulation than was afforded by the bakelite. A ring of bakelite attached to the smaller jar about 7 cm. below the cover afforded additional support to the tubes which insulated the leads, and also provided some thermal insulation for the chamber. No fan was provided for stirring the air in the chamber, since the heating and the cooling arrangements were such that convection could be relied upon to maintain a reasonably uniform temperature. The temperature at the center of the stack of specimens was determined by means of a thermocouple. This thermocouple was imbedded in an aluminum plate which was placed between the test units. Electrical measurements were made when the temperature at the center of the assembly was within 0.5° C. of the temperature of the bath.

Low relative humidity in the measuring chamber was assured by the use of anhydrous calcium chloride as a drying agent, and by the passage of a slow stream of carbon dioxide from a cylinder into the chamber. The carbon dioxide escaped through the annular spaces between the Pyrex glass insulating tubes and the brass rods, which served as leads and prevented the entrance of air or moisture into the measuring chamber.

Small electric heaters were placed around the Pyrex glass insulating tubes as an additional precaution against the condensation of frost on the leads when measurements were being made at low temperatures.

4. Means for Maintaining Constant Temperature

The chamber which was operated at 25° C. was mounted in a well stirred oil bath provided with thermostatic control. The thermostat operated with a double contact so that the bath was either heated or cooled according to the temperature of the room. The heating was obtained by means of an electrical heating unit, and the cooling by the use of a small pump which circulated cold water through a coil in the bath.

The chamber which was used over the wide range of temperatures could be mounted in either a liquid bath or an air bath. Liquid baths were used below 25° C., water cooled by ice being employed in the range 25° to 0° C., and alcohol cooled

by carbon dioxide snow in the range 0° to −75° C. The liquid bath had a volume of about 10 gallons, and was well insulated so that no difficulty was encountered in regulating the temperature to within 1° C. of that desired by adding ice or carbon dioxide snow as it was needed. A liquid bath was also maintained in the smaller cylinder of the measuring chamber and was kept at the same temperature as the main bath. With a cooling surface immediately above the specimens, it was possible to maintain them at a uniform temperature without a forced circulation of air in the chamber.

The air bath which was employed for heating the measuring chamber above 25° C. was provided with an electric heater, a circulating fan, and a bimetallic thermostat. It was well insulated and the temperature of the air in it could be maintained to within 1° C., of the desired temperature. When the measuring chamber was placed in this air bath, the smaller jar was simply filled with a thermal insulating material. In this case, the air in the chamber was sufficiently stirred by convection to maintain the specimens at a uniform temperature, since the heat was applied to the bottom and sides.

V. ELECTRICAL MEASUREMENTS

Two types of electrical measurements were made—one type was the primary measurements on specimens having ordinary electrodes; the other type was the relative measurements on specimens having perforated electrodes. The primary measurements were made at 25° C. and 1000∼ for the purpose of computing the dielectric constant and conductivity from the observed dimensions of the specimens and the measured capacitance and conductance, respectively. The dielectric constant thus obtained was used with the capacitance of a test unit of identical composition, but having perforated electrodes, to compute a shape factor for this test unit. This shape factor and the thermal expansion of the specimens were used to determine the dielectric constant and conductivity from the capacitance and conductance, respectively, measured between temperatures of −75° and 235° C. Though for making measurements over this extended temperature range, two different measuring chambers were used and different means were employed to secure the desired temperatures, the same method of assembling the specimens and making the electrical connections to them was employed throughout the investigation.

The electrical measurements which were made on the specimens were the capacitance, power factor, and conductance. The capacitance and the power factor were measured at five frequencies, and the conductance at two elapsed times after electrification. The methods used in part of the measurements have been described elsewhere, and will be only briefly sketched here. The dielectric constant and conductivity were computed from these measurements and the dimensions of the specimens.

1. Capacitance and Power Factor

The capacitance and power factor measurements at 60, 1000, and 3000∼ were made with the modified Rosa series inductance bridge, a diagram of which is shown in Fig. 4. A telephone receiver was used as the detector for 1000 and 3000∼, and a vibration galvanometer for 60∼. The manipulation of this bridge is described in the legend.

A modification of the resonance method described by Dellinger and Preston[10] was used to measure the capacitance and power factor at 100,000 and 300,000∼. A diagram of this set-up is shown in Fig. 5. The method of making the measurements is described in the legend.

The source of 60~ frequency was the local power circuit. The frequency of the power supply was so well controlled that it was sufficiently accurate for these measurements.

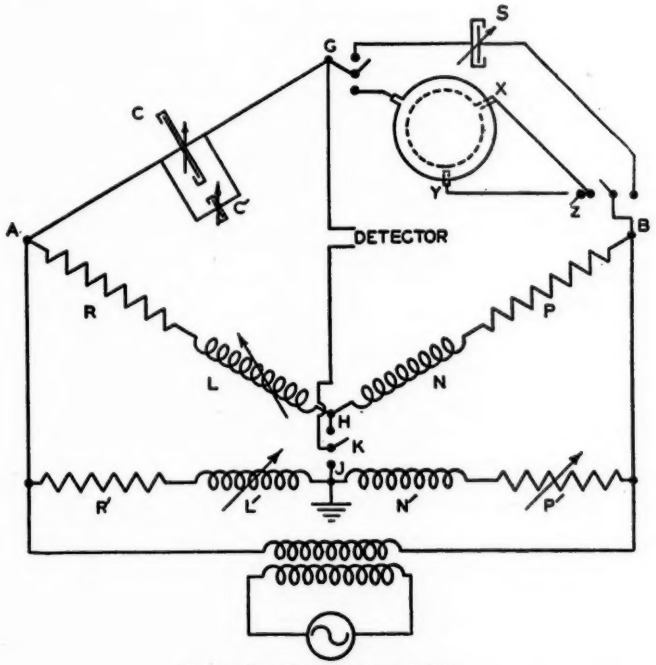

Figure 4—Modified Rosa Bridge

To make a measurement of capacitance and power factor several cycles of adjustment must be made in which the detector is connected first to the bridge and then to the Wagner earthing system. First connect the specimen in the bridge not only by its regular lead X but also by the dummy lead Y. The cycle consists in first connecting K to H and balancing by adjusting C and L, then connecting K to J and balancing by adjusting P' and L'. This cycle is repeated until the throwing of K from J to X does not affect the balance of the bridge or of the Wagner earthing system. Let the reading of the left-hand inductor be L_1. Connect a calibrated capacitor S into the bridge in place of the specimen and make another cycle of adjustments varying S instead of C. Let the readings of the calibrated capacitor and left-hand inductor be S_1 and L_2. Connect the specimen into the bridge as before with the exception of the dummy lead Y which is disconnected not only at Z, but also at the specimen. Adjust the bridge in the same way as when both leads were connected. Let the reading of the left-hand inductor be L_3. Again substitute the calibrated capacitor for the specimen and make the cycle of adjustments. Let the reading of the calibrated capacitor be S_2. The reading of the inductor will be L_2 as before. The capacitance of the dummy lead and hence of the measuring lead is $S_1 - S_2$. The capacitance of the specimen is $S_2 - (S_1 - S_2) = 2S_2 - S_1$. If $L_1 = L_3$ as is usually the case, and $R = P$, the power factor F is given with sufficient approximation by the equation

$$F = \frac{\omega(L_2 - L_1)}{R}$$

where ω is 2π times the frequency of the alternating current used in the measurement, and R and P are the total resistances of the arms AH and BH. If the lead capacitance is not to be determined, the first part of this procedure is omitted.

The frequencies of 1000 and 3000~ were obtained from a motor generator driven from a direct-current supply. At full speed this machine supplied a current at 3000~. It was run at one-third of full speed to obtain a current at 1000~. The use of a remote-control system and a frequency meter made it possible to con-

trol the 1000~ frequency with high accuracy. No frequency meter was available for use with the 3000~ frequency, but the generator was steady at full speed, and after being set with a tachometer and stop-watch, gave a frequency which was sufficiently accurate for purposes of the present investigation.

The radio frequencies of 100,000 and 300,000~ were obtained from a radio-frequency generator, using a 250-watt power tube in a tuned plate circuit. This generator was adjusted for the desired frequency and the output was checked at frequent intervals by means of a calibrated frequency meter.

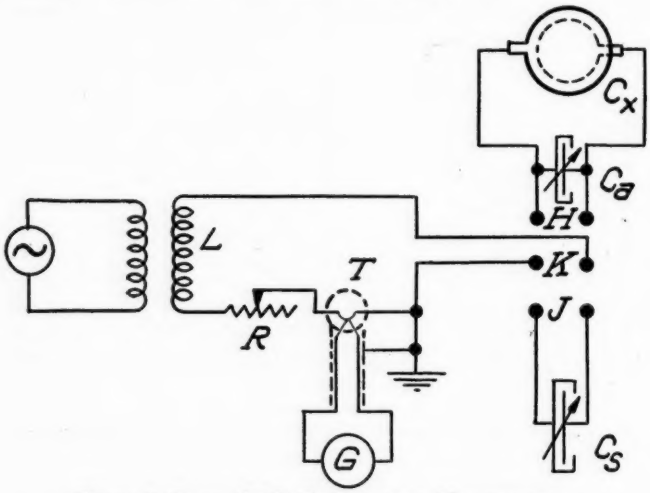

Figure 5—Set-up for Radio-Frequency Measurements

The set-up consists of an inductance coil L, a noninductive decade resistance R, and a vacuum thermocouple T connected in series to the midpoints K of a double pole, double throw switch by means of which the calibrated variable air capacitor C_s or the test unit C_x and parallel variable air capacitor C_a may be connected into the circuit. The measurement of capacitance and power factor consists in adjusting the circuit containing first the specimen and then the calibrated air capacitor to resonance with the source. The test unit is first introduced into the circuit by connecting K to H, R being set at zero resistance, and resonance is then obtained by adjusting C_a. The coil is so chosen that C_a will be small. The coupling between the source and the resonance circuit is so adjusted by moving the source that a large deflection of the galvanometer is obtained. The noninductive resistance R is then increased until the angular deflection of the galvanometer is decreased to one-fourth. Let this resistance be R_1. The capacitor C_s is introduced into the circuit by connecting K to J, R is set at zero resistance, and C_s is adjusted until resonance is obtained. The coupling is again adjusted to give a large angular deflection of the galvanometer, and then this deflection is decreased to one-fourth by increasing R. Call this resistance R_2. The capacitance of the specimen C_x is then $C_s - C_a$, where C_s is the capacitance of the calibrated air capacitor and C_a is the capacitance of the parallel air capacitor and the leads. The power factor is given with sufficient accuracy by the equation

$$F = \frac{\omega C^2_s (R_1 - R_2)}{C_x}$$

2. Dielectric Constant

The dielectric constant K of the medium of a capacitor is given by the equation:

$$K = \frac{C}{C_o} = AC \qquad (1)$$

where C is the measured capacitance, C_o is the capacitance which the capacitor would have if vacuum were its dielectric, and $A = \frac{1}{C_o}$ is the shape factor of the ca-

pacitor. The specimens having ordinary electrodes were so designed and prepared that C_o, and hence A could be computed from the measurements of the dimensions. For a test unit the value of C_o in micromicrofarads is given to a sufficient approximation by the equation:

$$C_o = \frac{A_1 d_2 + A_2 d_1 + 8rd^2[\ln 2 + (1 + x)\ln (1 + x) - x \ln x]}{11.31\ d_1 d_2} \qquad (2)$$

where A_1 and A_2 are the areas and d_1 and d_2 are the thicknesses of the individual specimens making up the test unit, d is the average of d_1 and d_2, r is the average of r_1 and r_2, which are the radii of the small electrodes of the two specimens, x is $\frac{t}{4d}$ where t is the total thickness of the two middle electrodes, and ln signifies the natural logarithm.[11] The dimensions are to be expressed in centimeters. This equation takes into account the edge effect, which is small.

As the computation of C_o and hence of A from measured dimensions is impracticable for test units having perforated electrodes, these test units were not used for primary determinations of the dielectric constant, but values of the dielectric constant were derived indirectly from measurements with them, a shape factor being determined for each test unit at 25° C. This shape factor was obtained from measurements of the capacitance of two test units of the same composition, one having ordinary electrodes and the other perforated electrodes. The dielectric constant of the rubber was calculated from the measurements on the test unit having ordinary electrodes. This value was used in conjunction with the capacitance of the test unit having perforated electrodes to obtain its shape factor. The test units having perforated electrodes were used for measurements over a wide range of temperature and frequency and the shape factors, corrected for the thermal expansion of the rubber, were used for the calculation of the dielectric constant.

3. Conductance

The conductance G of a test unit was determined by measuring, with a suitable apparatus, the current which flowed through the specimen under an applied electromotive force of known value. Since the value obtained for the conductance depended on the elapsed time between the application of the electromotive force and the measurement of the current, two different time intervals were used in this investigation—1 minute, which is the usual time in measurements of this sort, and a much shorter interval (about 0.002 second). The set-up for measuring the conductance at the end of 1 minute, which may be designated as the "1-minute" conductance, was the same as that described previously,[12] a self-explanatory diagram of which is shown in Fig. 6.

The "short-time" conductance, that is, the conductance obtained at the end of about 0.002 second, was measured with the aid of a Helmholtz pendulum, as shown diagrammatically in Fig. 7.

Though the time interval between the actions of S_2 and S_3 was usually 0.001 second, in some instances the conductance was so high that the galvanometer would deflect off the scale when this time interval was used, and in other instances the conductance was so low that the galvanometer deflection was too small to read. The deflection was made readable by shortening or lengthening the time interval between the actions of S_2 and S_3, though this affected the results, since the current was changing with time. For the highest conductance, this time interval was reduced to 0.0005 second, and the values obtained were higher than would have been obtained if the usual time interval had been employed. For the lowest conduc-

tances, the time interval was increased to 0.005 second, which made the results lower than they would have been had the usual time been employed. However, the results are usable, since high accuracy cannot be obtained in such measurements. All the "short-time" conductivity measurements are tabulated as though they were measured at 0.002 second after the potential was applied.

4. Conductivity

The conductivity γ of the material of a test unit was obtained by means of the equation:

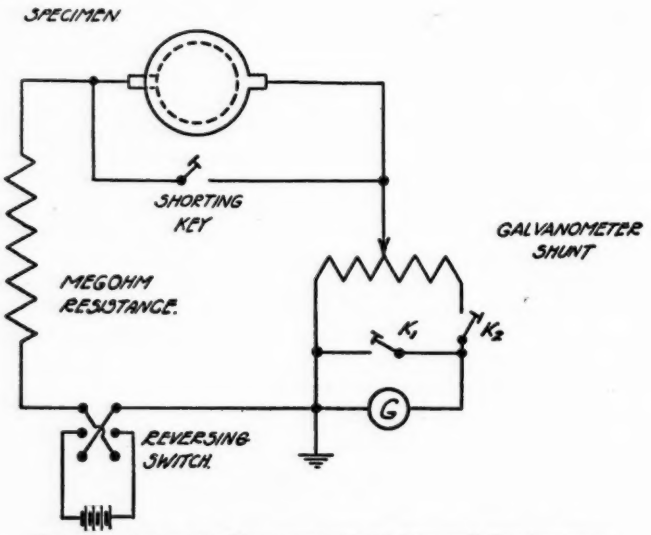

Figure 6—Set-up for Measuring the "1-Minute" Conductance

To make a measurement, the specimen is shorted, the shunt set at the lowest ratio, the reversing switch closed, and the deflection of the galvanometer noted when K_2 is closed. The deflection of the galvanometer is also noted when the reversing switch is thrown in the opposite direction. Call the average deflection d_m, the shunt ratio X_m, and the potential applied V_m. Next open the shorting key and obtain an average deflection as before, changing the shunt ratio until a readable deflection is obtained and using a higher potential if desired. The specimen must be shorted for two minutes between readings. Call the deflection at the end of one minute after the potential is applied d_x, the potential V_x, and the shunt ratio X_x. The conductance G is then given by the equation

$$G = \frac{d_x}{d_m} \cdot \frac{X_m}{X_x} \cdot \frac{V_m}{V_x} \cdot \frac{1}{10^6} \text{mho}$$

$$\gamma = BG \tag{3}$$

where G is the conductance of the test unit and B the shape factor for conductivity. The shape factor for conductivity is connected with the shape factor for dielectric constant by the equation:

$$B = \frac{A}{11.31} \tag{4}$$

where A is the shape factor for dielectric constant when the capacitance is measured in micromicrofarads. The shape factor for conductivity for each test unit at each temperature was obtained from the corresponding shape factor for the dielectric constant.

5. Accuracy of Determinations

The accuracy which can be assigned to the electrical constants of rubber of a definite composition depends not only on the accuracy with which the electrical and mechanical measurements can be made on a particular specimen, but also on

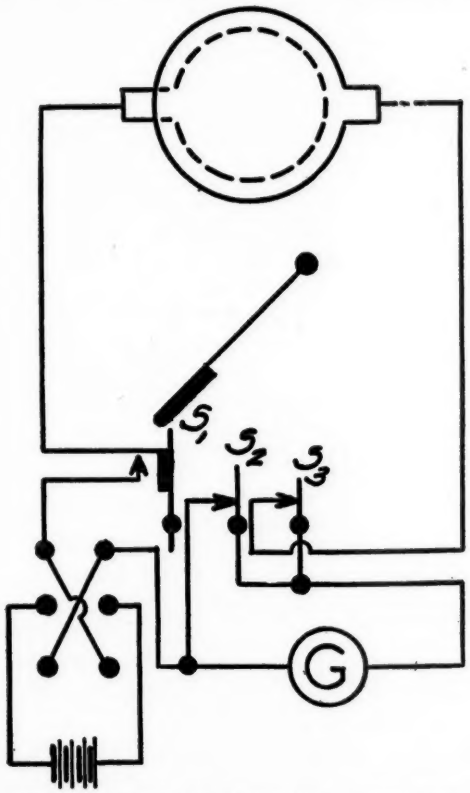

Figure 7—Set-up for Measuring "Short-Time" Conductance

The "short-time" conductance is measured with the aid of a Helmholtz pendulum. The specimen is connected into the circuit and the reversing switch closed. When the pendulum is released, it first strikes the prop from under S_1, allowing this switch to close. The pendulum then strikes S_2 0.0015 second later and opens it, which allows the current to flow through the galvanometer. The pendulum opens S_3 a predetermined time later (usually 0.001 second). The current which flows through the galvanometer between the openings of S_2 and S_3 gives a ballistic throw to the galvanometer. The conductance G is given by

$$G = \frac{Kd}{ET}$$

where K is the galvanometer constant, d is the ballistic deflection, E is the potential applied, and T is the time between the S actions of S_2 and s.

the accuracy with which specimens of a given composition can be reproduced at different times and from different lots of crude rubber. The accuracy of the measurements will be discussed in this section, while the reproducibility will be touched on briefly in subsequent divisions of the paper.

(*a*) *Effect of Errors in Dimensional Measurements.*—As already stated, the probable errors involved in the dimensional measurements are of the order of 1 or 2 per cent. These impose the chief limitation on the accuracy of the dielectric constant measurement. Conductance measurements on the other hand are subject to errors common to this type of measurement, of such magnitude that the accuracy of dimensional measurements is of relatively small importance. Power factor determinations are of course independent of the dimensions of the specimens.

(*b*) *Possible Sources of Error in Electrical Connections and Measurements.*—In the measurement of capacitance, care was taken to make the bridge errors as small as possible. The substitution method was used to eliminate from the measurements the capacitance between pieces of apparatus and between apparatus and ground. The errors in the bridge itself were considered to be negligible in comparison with other errors in the determination of dielectric constant.

It was necessary to make a correction for the capacitance of the leads which extended from the test unit to the outside of the constant temperature bath. The lead capacitance was not determined each time, but the average of a large number of determinations was taken as the capacitance of each lead. This average value did not differ from the measured value in any case by more than $5\mu\mu f$, which corresponds to a maximum error of 0.4 per cent in the determination of the capacitance of a test unit. The method of determining the lead capacitance is described in the legend under Fig. 4.

A possible source of error in the determination of the capacitance of a test unit resided in the fact that the individual members of the test unit did not necessarily have their small electrodes precisely in juxtaposition. But from the procedure used in assembling a test unit, it is unlikely that the centers of the small electrodes were out of line by as much as 1 mm. An eccentricity of this amount would give a maximum error of 0.3 per cent. As a matter of fact when several test units were repeatedly taken apart, reassembled and remeasured, the maximum variation in the capacitance which was observed was never greater than 0.2 per cent.

Contact resistances in the circuit were a potential source of error in the capacitance and power factor measurements. At the lower frequencies the errors due to any such resistances as may have been present were negligible, but at radio frequencies it was necessary to take special precautions to see that these resistances were so small that they did not cause any appreciable error. For these frequencies, all the metal parts were scraped before connections were made, and metal filings were put between each electrode and its connecting plate.

No guard rings were used in making any of the measurements, but it was unlikely that any significant errors arose from their omission because the specimens were kept in an atmosphere of low relative humidity while being measured.

(*c*) *Independent Determination of Dielectric Constant.*—A check was made on the determination of the dielectric constant of a few compounds at 25° C. by using an entirely different method for ascertaining it. The method consisted in measuring the dielectric constant by means of a parallel plate capacitor with a guard ring. Care was taken to have the guard ring at all times as near the potential of the guarded plate as possible. Measurements were made on a sheet of rubber prepared from the same batch as a pair of specimens which constituted a test unit. The sheet of rubber was placed between the parallel plates of the capacitor, and an air gap was left between the sheet and the upper plate. The bridge containing this capacitor was then balanced. The rubber sheet was removed from between the plates and the bridge was again brought to balance by changing the distance between the plates. The change in distance between the plates was determined

by making readings on an engraved scale with a telescope and micrometer eyepiece. The dielectric constant was then obtained from the equation:

$$K = \frac{t}{t - (d' - d'')} \tag{5}$$

where t is the thickness of the sheet of rubber and $(d' - d'')$ is the change in distance between the plates. Values of the dielectric constant obtained by this method agreed to within 2 per cent with those obtained by the other method.

(*d*) *Effect of the Condition of Electrode Surfaces.*—Some experiments were made to determine whether or not the condition of the electrode surfaces had any appreciable effect on the measured values of the capacitance and power factor. Such an effect has been reported for aluminum electrodes.[13] Several specimens were made up with aluminum electrodes which had been anodized (oxidized) like those used in that work. No appreciable difference was found between the values of the dielectric constant and power factor obtained with such electrodes and those obtained with ordinary electrodes.

VI. VALUES OF ELECTRICAL PROPERTIES

The measurements on rubber-sulfur compounds which are here reported show the effect of composition, temperature, and frequency on the electrical properties. From an experimental standpoint the results fall into two general groups. In the first group are the measurements at 25° C. on specimens having ordinary electrodes. In the second group are the determinations which were made over a range of temperatures and frequencies on specimens having perforated electrodes. The second group of measurements are dependent on the first, since a shape factor was obtained from capacitance determinations on specimens of identical composition having the two types of electrodes.

There is a further difference between the two groups of measurements in that the values reported for the electrical properties in the first group represent in most cases averages of several determinations, while those reported in the second group represent single determinations.

The primary measurements, which constitute the first group of results, were made at a single temperature, 25° C., and at a single frequency, 1000∼, and consequently these data can be summed up in one table or figure. The comparative measurements, however, were made at a number of temperatures and at several frequencies. To express these results concisely, tables and figures are given showing the relation of the electrical properties to two simultaneous variables—composition and temperature. The effect of the third variable, frequency, is shown by giving separate tables and figures for each frequency.

1. Electrical Properties at 25° C.

Electrical measurements at 25° C. were made on compounds of purified rubber and sulfur covering the range from unvulcanized rubber to completely vulcanized hard rubber. Twenty-two different compositions were employed, spaced at intervals of 0.5 to 2.0 per cent sulfur to define precisely the changes in electrical properties with composition. From 1 to 16 different test units or pairs of specimens of each composition were prepared and measured, the average number being 7. Dielectric constant and power factor measurements were made at 1000∼, and the conductance measurements were made 1 minute after the application of potential to the specimen.

The results are shown graphically in Fig. 8, in which the three electrical properties are plotted as functions of the composition expressed as per cent of sulfur. Each of the properties has characteristic features, but it should be noted that each has a maximum at some composition.

(*a*) *Dielectric Constant.*—The dielectric constant of unvulcanized rubber was found to be 2.37. With increasing sulfur content, the dielectric constant increased almost linearly to a maximum of about 3.75 in the neighborhood of 11.5 per cent sulfur. With larger sulfur content, it decreased rapidly and reached a minimum of 2.70 at about 22 per cent sulfur. Above 22 per cent sulfur, there was a slow increase in dielectric constant, and a value of 2.82 was observed for rubber containing 32 per cent sulfur.

The average deviation of individual dielectric constant determinations from the mean of those of the same composition, made under identical conditions, was less than 1 per cent in the majority of cases.

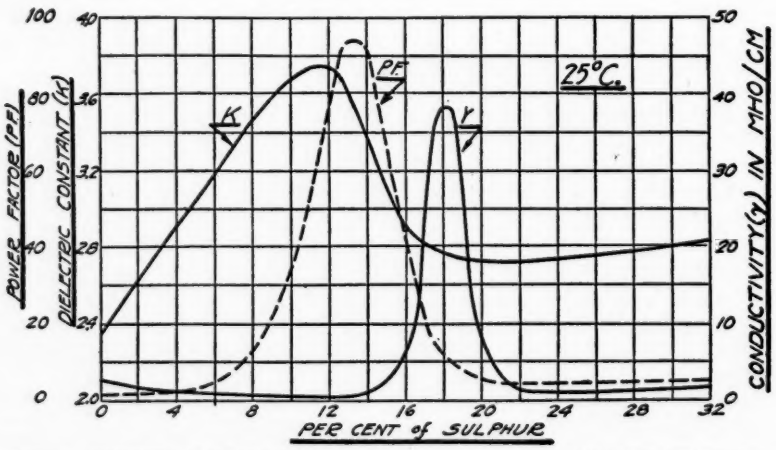

Figure 8—Relation of the Dielectric Constant, Power Factor, and "1-Minute" Conductivity of Rubber-Sulfur Compounds to the Per Cent of Sulfur

The power factor is given in units of 1×10^{-3} and the "1-minute" conductivity in units of 1×10^{-17} mho/cm.

(*b*) *Power Factor.*—The power factor of unvulcanized rubber was 1.6×10^{-3}. There was a slow decrease in power factor up to about 4 per cent sulfur, and above this composition the increase became relatively rapid until a maximum of 93.8×10^{-3} was reached at about 13.5 per cent sulfur. With further increase in sulfur content, the power factor decreased rapidly and reached a minimum value of 2.6×10^{-3} at about 23 per cent sulfur. Throughout the range of hard rubber compounds the power factor increased slowly and attained a value of 5.1×10^{-3} for 32 per cent sulfur.

The average deviation of power factor determinations from the mean of each composition amounts to as much as 30 per cent in some instances, and is 11 per cent for the group as a whole. Since probable errors in measurement amount to less than 5 per cent for the lower power factors and to less than 1 per cent for the higher power factors, this deviation from the mean may be attributed to the possible effect of incidental impurities which, in small proportion, may materially alter the power factor of a dielectric.

(c) *Conductivity.*—The curve relating "1-minute" conductivity to composition is similar to the curve for the power factor in that both show similar sharp and high maxima. The conductivity of unvulcanized rubber is 2.3×10^{-17} mho. per cm. This decreases with increasing sulfur content and reaches a minimum value of 0.5×10^{-17} at about 12 per cent sulfur. Above this minimum a sharp increase takes place, and at 18 per cent sulfur there is a maximum conductivity of 38×10^{-17}.

Beyond the maximum there is an equally sharp decrease, so that at 22 per cent sulfur the conductivity is only 1×10^{-17}. Above this point, throughout the hard rubber range, the conductivity increases very slightly.

The variation in conductivity between individual samples of the same composition is considerable, as would be expected from the nature of the results that are obtained in conductivity measurements on dielectrics in general. This variation is as much as 70 per cent in one instance, and is on the average 31 per cent. A negligible part of this variation is doubtless attendant on circumstances having to do with the dimensional or electrical determinations, but most of it is probably due to slight accidental variations in the composition of the rubber.

2. Measurements at −75° to 235° C.

The measurements which were carried out to determine the effect of temperature and frequency on the electrical properties covered the range from −75° to 235° C. at intervals of about 10° and were made at five frequencies, namely, 60, 1000, 3000, 100,000, and 300,000∼. The conductivity was measured at two time intervals after the application of potential, namely 0.002 second and 1 minute. The compositions on which the measurements were made covered the range of possible rubber-sulfur compounds at slightly wider intervals than the previous series of measurements at 25° C., there being 14 instead of 22 different percentages of sulfur. As has been indicated previously, these specimens were all made with perforated aluminum sheets as electrodes, and, instead of measuring the thickness and area, a shape factor was determined and was used in computing the dielectric constant and conductivity values.

For specimens containing not over 12 per cent of sulfur, the test units used above 25° C. were not the same as those used below 25° C., but for higher percentages of sulfur each test unit was used throughout the entire range of temperature.

Only a single pair of specimens constituting a single test unit of each composition was used, but the consistency of the change in electrical properties with temperature and frequency affords a reasonable indication that there were no large experimental errors.

Measurements are here reported for temperatures between −75° C. and the highest temperature at which accurate measurements could be made. The lower limit was fixed by the lowest temperature which could be readily maintained with carbon dioxide snow. The upper limit was different for different samples, depending either on the decomposition of the sample during the time the observations were in progress, on its change in shape because the sample began to flow, or on its increase in conductivity. The samples were generally measured at temperatures higher than herein reported, the upper limit for reporting results being fixed after the measurements were completed.

In determining the temperature at which a sample had deteriorated to a point where the results should not be reported, the decision was made that, when a sample had lost an amount of sulfur equal to 0.3 per cent of the original weight of the sample, it was no longer representative. Using the results of Cummings,[14] the temperatures were determined at which the samples of each composition would lose this

amount of sulfur under the conditions at which the electrical measurements were made; namely, increasing the temperature in steps of 10° or 20° and maintaining the specimens at each temperature for 8 hours. A change in shape caused by the

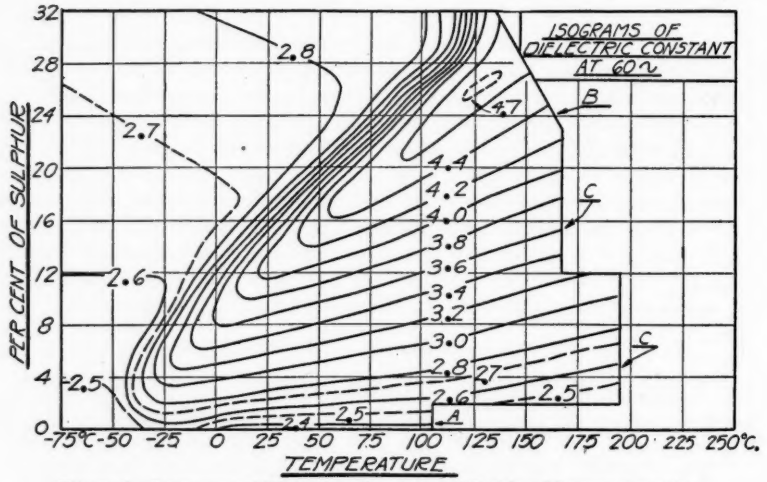

Figure 9—Isograms of Dielectric Constant of Rubber Measured at 60~

Each line connects points having equal values of dielectric constant.
A is the temperature limit set by the flow of the specimen. *B* is the temperature limit set by the decomposition of the specimens. *C* is the temperature limit set by the high conductance.

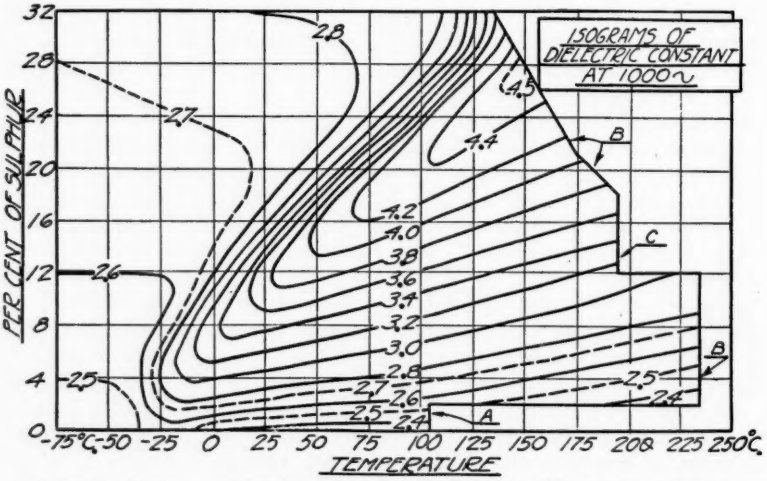

Figure 10—Isograms of the Dielectric Constant of Rubber Measured at 1,000~

For meaning of symbols see Figure 9.

flowing of the material of the sample affected only the one having 0 per cent sulfur. It is known that such material flows readily at temperatures above 105° C. A temperature limit was imposed by the increase in the conductivity of certain samples because neither it nor its accompanying power factor could be measured

without a redesign of the apparatus, which did not seem to be necessary. The figures show which one of these causes decided the upper limit.

The effect of the temperature on the relation between electrical properties and the composition is shown by the use of contour charts, in which temperature and

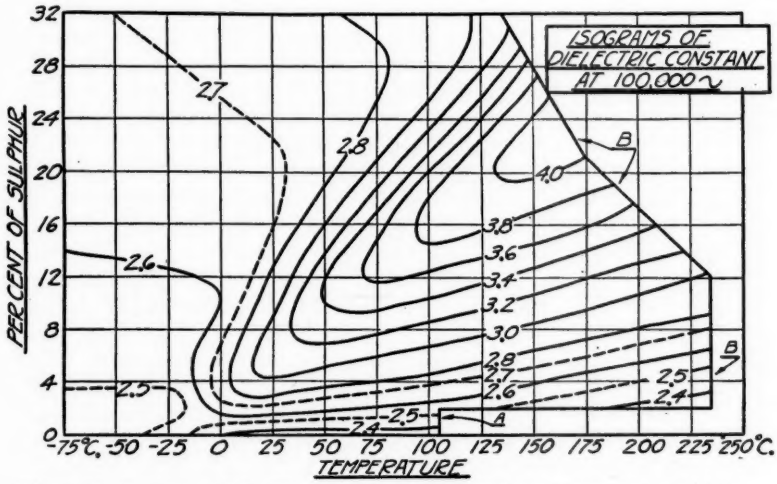

Figure 11—Isograms of the Dielectric Constant of Rubber Measured at 100,000~

For meaning of symbols see Figure 9.

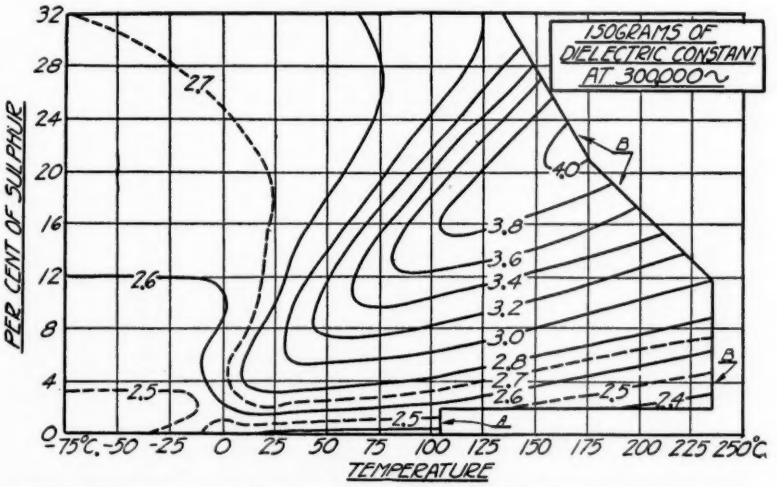

Figure 12—Isograms of Dielectric Constant of Rubber Measured at 300,000~

For meaning of symbols see Figure 9.

composition are abscissa and ordinate, respectively, while the electrical properties are represented by isograms which may be visualized as the contour lines of a solid model. The subsequent discussion will refer to the charts as representations of such models. While the model for each property has distinctive features, they

have one feature in common, namely, a prominent diagonal ridge in which each property goes through a maximum.

(*a*) *Dielectric Constant.*—The variations of the dielectric constant with composition and temperature at different frequencies are shown in Figs. 9 to 12. The

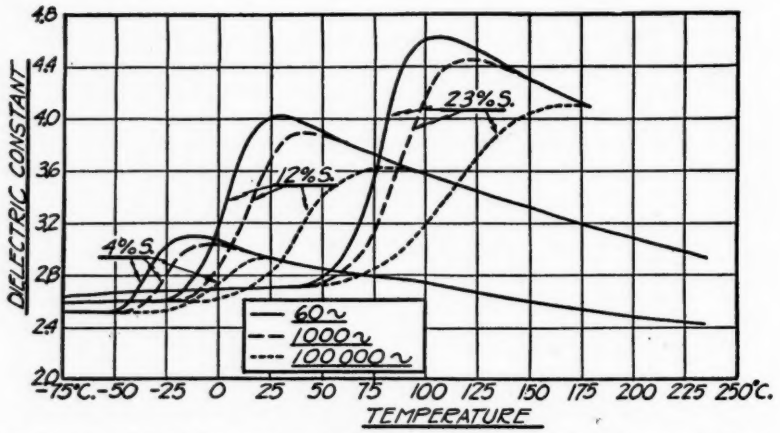

Figure 13—Effect of Frequency and Temperature on the Dielectric Constant of Rubber-Sulfur Compounds Containing 4, 12, and 23 Per Cent Sulfur

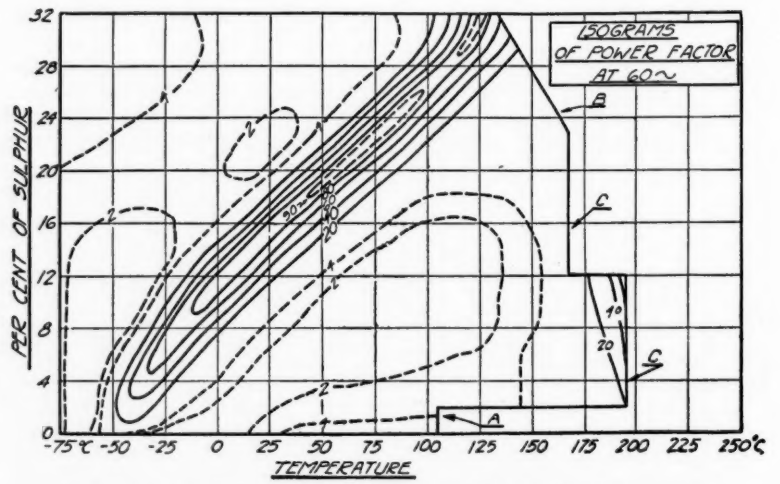

Figure 14—Isograms of the Power Factor of Rubber Measured at 60~

Each line connects points having the same value of power factor. The values are given in units of 1×10^{-3}.

A is the limit set by the flow of the specimen. *B* is the limit set by the decomposition of the specimen. *C* is the limit set by the high conductance of the specimen.

results at 3000~ are not shown graphically because of close similarity to results at 1000~.

All of the charts have as a prominent feature the diagonal ridge which was mentioned previously. This ridge increases in height from low to high percentages

of sulfur. On the low temperature side of the ridge, there is a steep slope which falls away to an almost level area. This level area represents a region in which the dielectric constant changes little with composition and temperature. On the

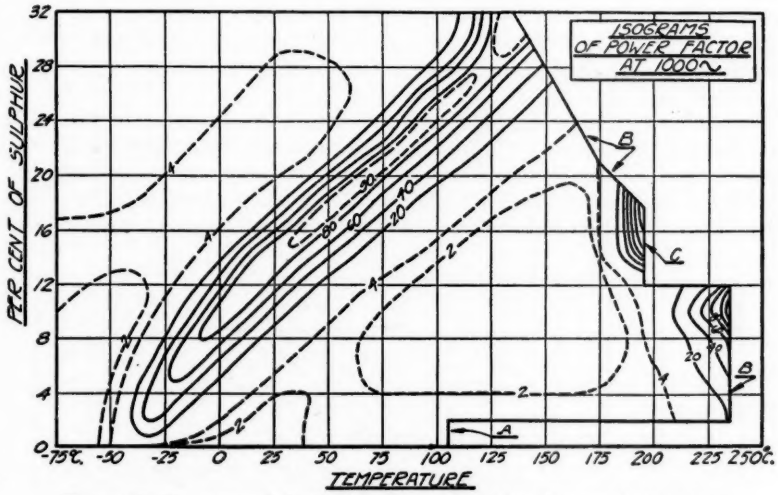
ISOGRAMS OF POWER FACTOR AT 1000~
PER CENT OF SULPHUR
TEMPERATURE
-75°C. -50 -25 0 25 50 75 100 125 150 175 200 225 250°C.
0 4 8 12 16 20 24 28 32
A
B
C

Figure 15—Isograms of the Power Factor of Rubber Measured at 1,000~

For meaning of symbols see Figure 14.

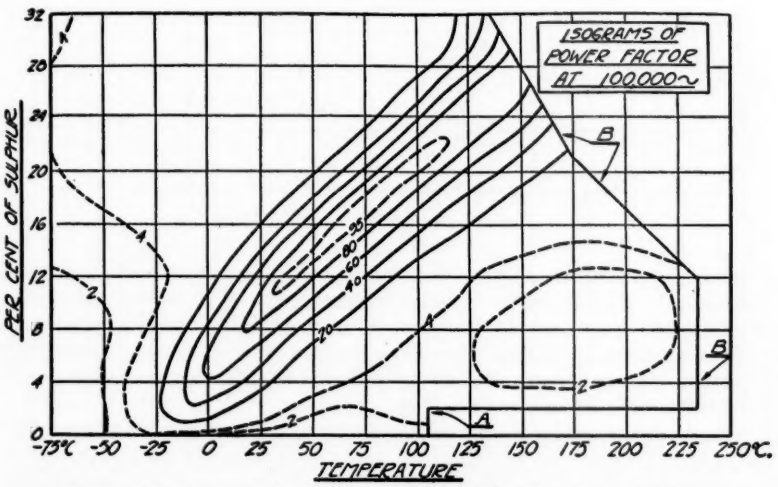

Figure 16—Isograms of the Power Factor of Rubber Measured at 100,000~

For meaning of symbols see Figure 14.

high temperature side of the ridge, the slope is gradual and fairly uniform. In this region the dielectric constant decreases with rising temperature and increases as the percentage of sulfur becomes larger.

A change of frequency changes the height and position of the maximum or ridge,

and changes the steepness of the slope on the low sulfur side of the ridge. Increasing the frequency has the effect of shifting the maximum to lower percentages of sulfur and to higher temperatures. In other words, with increasing frequency, the diagonal ridge is displaced toward the right of the chart. The height of the maximum becomes less as the frequency is increased, *i. e.*, the rate of change of the dielectric constant with composition and temperature is less rapid the higher the frequency. The regions on either side of the ridge are affected relatively little by changes in frequency.

The composition-temperature relation shown in the isograms in Figs. 9 to 12 may also be represented for particular rubber-sulfur compounds, as in Fig. 13, where the dielectric constants at 60, 1000, and 100,000~ are plotted against the temperature for compounds containing 4, 12, and 23 per cent of sulfur. The relation of the curves for a single frequency indicates not only the manner in which

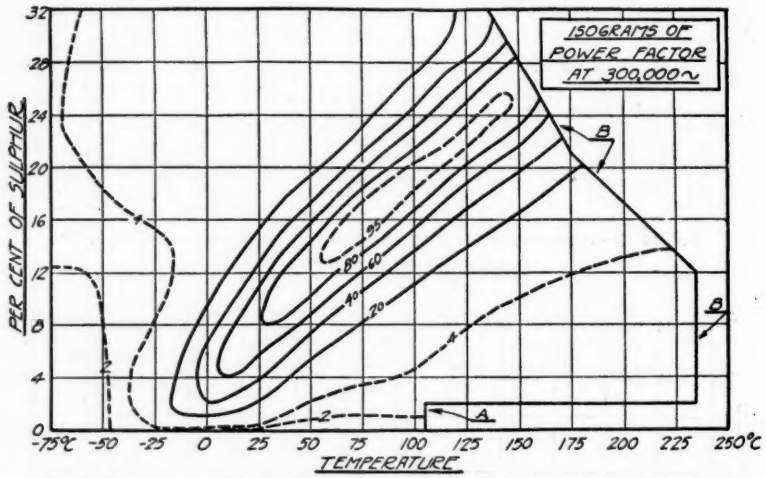

Figure 17—Isograms of the Power Factor of Rubber Measured at 300,000~

For meaning of symbols see Figure 14.

with increasing sulfur, the value of the maximum of the dielectric constant increases, but also how its position shifts to higher temperatures. It is on account of this shift in position that the curves for the compounds containing the highest percentages of sulfur do not reach maxima below temperatures at which decomposition becomes appreciable. These curves also show clearly how the maxima move to higher temperatures with increasing frequency.

(*b*) *Power Factor.*—The results which show the relation of power factor to composition and temperature are given in isograms in Figs. 14 to 17 for four of the frequencies, the chart for 3000~ being omitted because of its similarity to the chart for 1000~.

The charts are characterized by a prominent diagonal ridge, similar in position to that for the dielectric constant. There are, however, two differences between the charts for the power factor and for the dielectric constant. Approximately level areas in which the power factor is little affected by changes in either temperature or composition occur not merely on one but on both sides of the ridge, and on the high temperature side of the chart there is the beginning of a steep upward

slope which in some cases is not shown, as thermal decomposition sets the limit at a lower temperature.

A comparison of the isograms in Figs. 14 to 17 shows that a change in frequency has the same type of effect on the power factor as on the dielectric constant in that

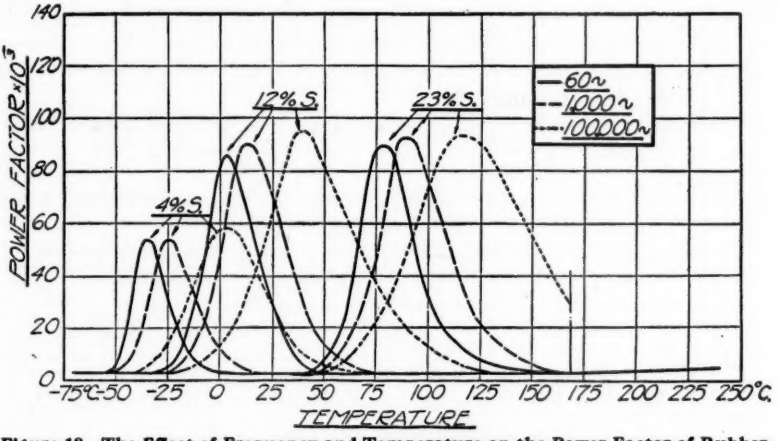

Figure 18—The Effect of Frequency and Temperature on the Power Factor of Rubber-Sulfur Compounds Containing 4, 12, and 23 Per Cent of Sulfur

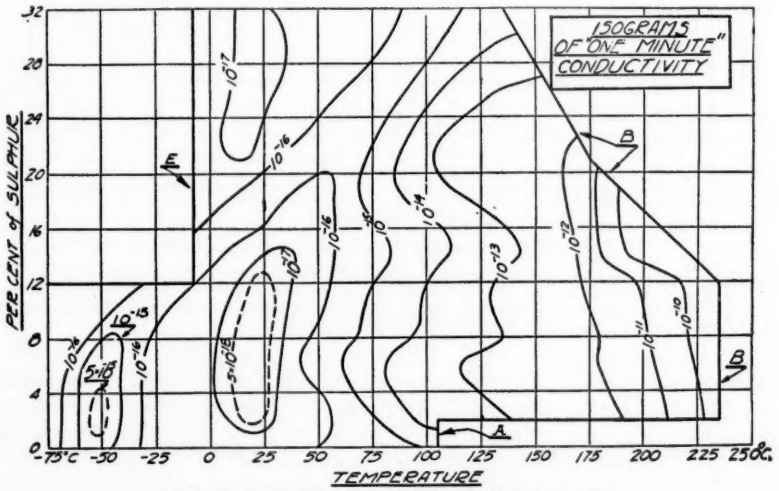

Figure 19—Isograms of "1-Minute" Conductivity

Each line connects points having equal values of the conductivity. The values are given in mho/cm. *A* is the limit set by the flow of the specimen. *B* is the limit set by the decomposition of the specimens. Measurements were not recorded below *E* because of difficulties with the apparatus.

the characteristic diagonal ridge is shifted toward the high temperature side of the diagram with increasing frequency. The steepness of the slopes on both sides of the ridge becomes less with increasing frequency. Unlike the dielectric constant for the same compound, increase of frequency does not change the height of the maximum very much, and apparently increases it rather than decreases it.

The relation of power factor to temperature and composition may also be illustrated for particular compositions as in Fig. 18, where the power factors at 60, 1000, and 100,000∼ are plotted against the temperature for compounds containing 4, 12, and 23 per cent sulfur. The height of the maximum at a single frequency increases rapidly with sulfur content up to about 12 per cent of sulfur. Further increase of the sulfur content does not materially change the height. The position of the maximum is shifted to higher temperatures as the sulfur content is increased. These curves also show the manner in which the maxima move to higher temperatures with increasing frequency.

(*c*) *Conductivity.*—The data pertaining to the effect of composition and temperature on the conductivity are given in the form of isograms, in Figs. 19 and 20, respectively.

The chart for the "1-minute" conductivity somewhat resembles similar charts

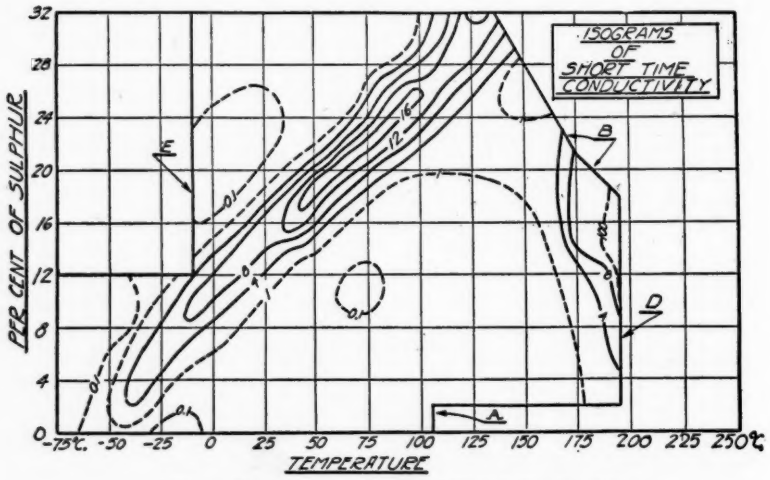

Figure 20—Isograms of "Short-Time" Conductivity

Each line connects points having equal values of conductivity. The values are given in units of 1×10^{-12} mho/cm. *A* is the limit set by flow of specimen. *B* is limit set by decomposition of specimen. *D* is limit set by range of apparatus. Measurements were not recorded below *E* because of difficulties with the apparatus.

for the power factor and dielectric constant in spite of the fact that it has been necessary to use a different kind of scale in spacing the isograms; that is, using a power of 10 between isograms instead of a fixed numerical difference. The diagonal ridge is fairly well defined. Along most of its length, it rises to an approximately uniform height of a little more than 10^{-16} mho per cm., but at its low sulfur end it goes to above 5×10^{-15} mho per cm. at $-50°$ C. There is a decided increase of conductivity with temperature above 25° C., and this increase makes difficult the location of the ridge at high percentages of sulfur. For many specimens, the conductivity at 225° C. is 10,000,000 times that at 25° C. Since measurements were made on a single set of specimens, and small amounts of impurities may cause considerable variation in the conductivity, precise significance should not be attached to minor features or irregularities in the isograms.

The "short-time" conductivity chart bears a closer resemblance to the power factor than to the "1-minute" conductivity chart. The diagonal ridge is high

and well defined, and it has steep slopes. On either side is located an area of low conductivity where changes in temperature or composition produce little effect. At low temperatures and low percentages of sulfur, the ridge almost disappears, but with rising temperature and increasing sulfur content the ridge reaches a height of about 100 times that of the low conductivity area on either side. As in the case of the power factor, the upward slope becomes evident only at the very edge of the chart on the high temperature side. Its similarity to the chart of 60-cycle power factor is particularly marked. The ridge falls at the same place on both, suggesting a possible connection between the "short-time" conductivity and the 60-cycle power factor. This will be studied further.

A comparison of the "short-time" and the "1-minute" conductivities for one compound containing 12 per cent of sulfur is shown on a semilogarithmic scale in Fig. 21. This figure indicates that the "short-time" conductivity is considerably higher than the "1-minute" conductivity at ordinary temperatures, but that the two approach and become very nearly the same at the highest temperatures used

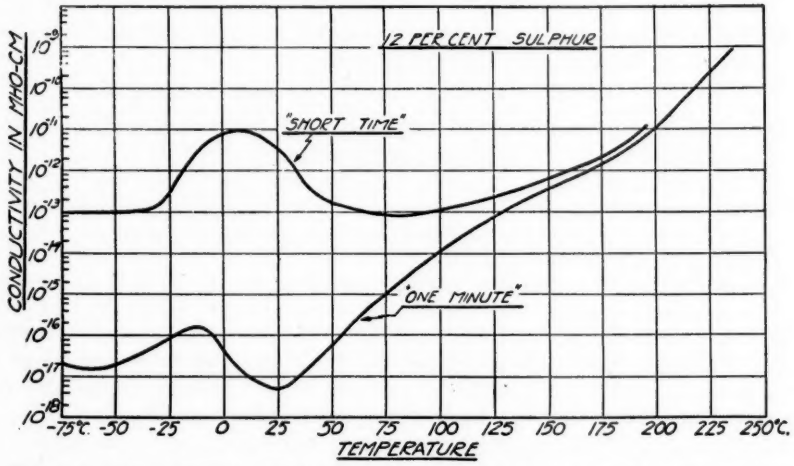
12 PER CENT SULPHUR
"SHORT TIME"
"ONE MINUTE"
CONDUCTIVITY IN MHO-CM
TEMPERATURE
-75°C. -50 -25 0 25 50 75 100 125 150 175 200 225 250°C.

Figure 21—"Short-Time" and "1-Minute" Conductivities for a Rubber Containing 12 Per Cent of Sulfur

in the measurements. Comparison of the two conductivities for other compositions led to similar conclusions.

VII. COMPARISON OF ELECTRICAL PROPERTIES OF COMPOUNDS OF PURIFIED RUBBER AND SULFUR WITH THOSE OF CRUDE RUBBER AND SULFUR

A comparison of the results reported in this paper with those previously reported for crude rubber indicates that purification of the rubber has only a relatively small effect on the dielectric constant and power factor, and a larger effect on the conductivity. The curves in Fig. 8 were made under the same conditions as the curves in Figs. 8, 9, and 10 of our previous paper on crude rubber.[15] The curve of dielectric constant for compounds of purified rubber is slightly lower than the corresponding curve for crude rubber, except that the maximum value at about 11 per cent of sulfur is the same (3.75) for the two. The values of the dielectric constant for purified rubber specimens are, on the average, about 0.06 lower than those of the corresponding crude rubber specimens on the low sulfur side of the

maximum and about 0.08 lower on the high sulfur side of the maximum. The maxima of the two curves occur at the same composition for both.

The power factors of the purified rubber specimens are lower than those of the corresponding crude rubber specimens except in the region of the maximum, where the power factor of the purified rubber appears to rise to a higher maximum than that of crude rubber. In the regions of low and of high per cent of sulfur, the power factors of specimens of purified rubber are generally 30 to 50 per cent less than those of crude rubber.

The conductivity of purified rubber is not so readily compared with that of the previous work on crude rubber, since in the previous paper the resistivity was plotted instead of the conductivity. A comparison of values shows that the conductivity of crude rubber is from 5 to 20 times as much as the corresponding specimens of purified rubber excepting in the region of the maximum, where there seems to be little difference between the two.

The values for the dielectric constant and power factor of crude rubber as determined by Kitchin[16] and by Kimura[17] and his associates are appreciably larger than those herein reported. The curves which they give indicate that purification of the rubber does not change the temperature or the frequency at which either the dielectric constant or power factor is a maximum.

VIII. SELECTION OF RUBBER COMPOUNDS FOR SPECIFIC USES

The properties of rubber and its compounds with sulfur have a direct bearing on many practical problems because such sulfur compounds form the basis of virtually all commercial rubber products. While the commercial rubber products are usually compounded with fillers and other ingredients which affect the electrical properties of the product, the effects of these are superimposed on the basic properties of the rubber-sulfur compounds.

If rubber of low dielectric constant is required, as for the insulation of submarine telephone or telegraph cables, an inspection of isograms in Figs. 9 to 12 indicates clearly that the best results are to be obtained with the lowest practicable proportion of combined sulfur. For example, at 25° C. and 1000$\sim$ the rubber alone has a dielectric constant of 2.4; with 1 per cent of combined sulfur, the dielectric constant is about 2.5, and with 3 per cent of sulfur it is about 2.8. If a dielectric constant less than 2.8 is necessary, percentages of combined sulfur less than 3 per cent must be used. If it is desirable that the insulation have the mechanical properties of the high sulfur or hard-rubber range, a dielectric constant as low as 2.75 can be obtained. The use of the minimum per cent of sulfur in such cases is in accordance with recent developments in cable engineering,[18] some of which have resulted from this investigation.

When a low power factor is needed, the frequency used must be taken into account. At 60$\sim$ and 25° C., specimens containing up to 8 per cent of combined sulfur have power factors of less than 4×10^{-3}, but the range of composition having this low power factor at 300,000$\sim$ lies below 1 per cent of combined sulfur. About as low a power factor can be obtained with high sulfur content; that is above 20 per cent at 60$\sim$. However, the power factor in this range of composition increases but little with frequency rising to about 8×10^{-3} at 25° C. and 300,000$\sim$.

The results show that purification of the rubber makes it possible to obtain soft rubber having as low conductivity as hard rubber, whereas if the rubber is not purified the soft rubber has much higher conductivity than the hard rubber. It is of advantage, then, to purify the rubber when a low conductivity is desired. If the rubber is purified, it makes little difference, as far as conductivity at 25° C.

is concerned, what composition is used with the exception of the range from 14 to 24 per cent of sulfur, where the conductivity is definitely higher.

The conductivity of rubber does not necessarily increase with temperature as is usually assumed in the preparation of tables and formulas which are used in specifications for correction of temperature. This is clearly shown by Fig. 19. It may either increase or decrease according to the temperature range used. For instance, the conductivity of a specimen containing 8 per cent of sulfur decreases with temperature from 0° C. to about 20° C. and then increases as the temperature is increased above this. This indicates quite clearly the inadequacy of the usual formulas for correcting the conductivity or resistivity for differences in temperature.

IX. CONCLUSION

The electrical measurements given in this paper differ from those previously reported by the authors and by other investigators in that they were made on specimens prepared from purified rubber. The purification, which involved the removal of proteins, resins, and water-soluble salts, affected all the electrical properties to some extent, but did not alter the general character of the variation in electrical properties with composition, temperature, or frequency.

The results of the present investigation afford comprehensive data on the electrical properties of rubber-sulfur compounds, and may form a basis for designing rubber compounds for specific electrical uses. They also demonstrate the inadequacy of the simple numerical coefficients that are sometimes employed to evaluate the changes in the electrical properties with temperature and frequency.

A discussion of the results from the standpoint of modern dielectric theory is not included in the present paper, but is contemplated for a separate paper.

X. ACKNOWLEDGMENT

Acknowledgment is made of the important assistance which A. D. Cummings rendered in preparing many of the specimens used in this investigation and in helping with some of the electrical measurements.

[1] *Bur. Standards Sci. Papers*, **22** (S560), 398 (1927).

[2] Dielectric Properties of the Rubber–Sulfur System, *Inst. Elec. Engrs. J.* (Japan), pp. 1274–1277, December, **1928**.

[3] Kitchin, *Am. Inst. Elec. Engrs. J.*, **48**, 495 (1929).

[4] The Specific Gravity and Thermal Expansion of the Rubber–Sulfur System, *Soc. Chem. Ind. J.* (Japan), Supplemental Binding, **32**, 196B (1929).

[5] McPherson, A Method for the Purification of Rubber and Properties of Purified Rubber, *Bur. Standards J. Research* (RP449), **8**, 751 (1932); RUBBER CHEM. & TECH., **5**, 523 (1932).

[6] See footnote 1 (p. 174) and also Curtis and McPherson, Dielectric Constant, Power Factor, and Resistivity of Rubber and Gutta-Percha, *Bur. Standards Tech. Papers*, **19**, 669 (1925).

[7] F. H. Rolt, *Gages and Fine Measurements*, Vol. 1, p. 339. The Macmillan Co., New York, **1929**.

[8] See footnote 4.

[9] See reference in footnote 1.

[10] Methods of Measurement of Properties of Electrical Insulating Materials, *Bur. Standards Sci. Papers*, **19** (S471), 39 (1923). The method here referred to is described on p. 43.

[11] Gunthershulse, Measurement of the Dielectric Constant and Dipole Moment, *Handbuch der Physik.*, Vol. **16**, Chap. 20.

[12] Curtis and McPherson, Dielectric Constant, Power Factor, and Resistivity of Rubber and Gutta-Percha, *Bur. Standards Tech. Papers*, **19**, 669. The set-up here referred to is described on p. 678.

[13] Curtis, The Dielectric Constant of Liquid Sulfur, *J. Chem. Phys.*, **1**, 160 (1933). Curtis obtained temperature curves of dielectric constant and power factor similar to those which were obtained for rubber, but the values were not the same on different runs. When the aluminum electrodes were anodized, quite different curves were obtained which could be readily reproduced.

[14] *Bur. Standards J. Res.*, **9**, 163 (1932); RUBBER CHEM. & TECH., **6**, 46 (1933).

[15] See reference in footnote 1, p. 411.

[16] *Ind. Eng. Chem.*, **24**, 549 (1932); RUBBER CHEM. & TECH., **5**, 367 (1932).

[17] See footnote 2.

[18] Rowand, Part I, Davis and Crowdes; Part II: Submarine Telephone Cable. *Electrician*, **107**, 721 (1931); Kemp, "Paragutta, a New Insulating Material for Submarine Cables," *Bell System Tech. J.*, **10**, 132 (1931); *J. Franklin Inst.*, **211**, 37 (1931).

[Reprinted from Industrial and Engineering Chemistry, Vol. 25, Pages 1096–1101, October, 1933.]

Effect of Temperature on Tensile Properties of Vulcanized Rubber

A. A. Somerville and W. F. Russell
R. T. Vanderbilt Company, Inc., New York, N. Y.

The tensile properties and tear resistance of a large number of commercial inner tubes, before and after aging by different methods, are studied at 0°, 25°, and 100° C. A number of uncured bus-truck tube stocks are also studied from the point of view of their capacity to withstand high temperatures.

The effect of testing rubber at 100° C. as compared with room temperature is discussed; how some compounds collapse at 100° C., while others have tensile properties equal to, or better than those at 25°, is shown. The effect of testing artificially aged specimens at 100° C., as well as at 25° C., is discussed; the high-temperature test may reveal conditions of deterioration and overcure that are not noticeable in the 25° tests. The compounding and curing conditions that lead to high tensile properties at 100° C., as well as those which cause inferior quality, are discussed.

THE amount of published data on the physical properties of vulcanized rubber at widely different temperatures is meager considering the wide range of temperatures over which rubber products are expected to give service. Temperature variations due to seasonal causes alone are large, but these may be greatly accentuated in rubber articles such as tires, tubes, fan belts, and motor mounts, by severe conditions of service. An understanding of the behavior of vulcan-

ized rubber at widely different temperatures, and particularly at high temperatures, is therefore becoming more and more essential for the development of suitable compounds for rubber particles that must withstand large temperature variations.

Previous Work

A report in 1926 by van Rossem and van der Meijden (*3*) on the influence of high temperatures on the stress-strain curve of vulcanized rubber was the first systematic attack upon this problem. These investigators did not use commercial compounds but a pure gum mix (92.5 rubber, 7.5 sulfur by weight). Tests were made at temperatures from 24° to 147° C. It was found that, as the temperature increased, the stress-strain curve shifted progressively toward the elongation axis—i. e., the rubber softened; that the amount of shift was further influenced by the degree of vulcanization and the time of heating; that the tensile strength reached a maximum at about 70° C. and then decreased; that higher temperatures imparted brittleness to the rubber, which disappeared on cooling—i. e., was not apparent in room temperature tests; and that the brittleness appeared in cures with high vulcanization coefficients sooner than in those with low coefficients. The authors suggested that high-temperature testing might be considered as a method of artificial aging. A further communication in 1927 by the same authors (*4*) deals with changes in the stress-strain curve, hardness, and plasticity of vulcanized rubber heated up to 147° C.

Breuil (*1*) in 1910 gave data on four compounds (including ebonite) over a range of −10° to +100° C. Le Blanc and Kroeger (*2*) in 1926 gave some data on the effect of low temperatures, chiefly on rubber-sulfur mixes, and concluded that the presence of organic accelerators did not materially affect their results.

The U. S. Bureau of Standards (*6*) in 1928 published data giving physical tests on six different types of rubber compounds at temperatures from −70° to +147° C. The results showed that at very low temperatures the specimens became rigid, with greatly increased tensile strength which gradually decreased with rising temperature until, at 147° C., it became practically negligible. All six compounds showed the same type of behavior, and it was concluded that the differences due to compounding ingredients were differences in degree rather than in kind.

In 1928 Somerville and Cope (*5*) published results on the effect of temperature on the stress-strain properties of several different types of laboratory compounds. It was shown that wide variations appeared in the stress-strain curves of the same stock at different temperatures; that there was a progressive drop in the stress values as the temperature was raised from 0° to 100° C.; that the amount of sulfur used was a factor in the stress-strain relationship at different tem-

peratures; that the stress-strain properties at different temperatures varied for different rubbers; that the state of cure caused a wide variation in tests at different temperatures; that successive stretchings of the same specimen caused large decreases in the stress after the first or second cycle; that stripping tests on frictions showed much lower strength at 100° than at 0° C.; and that overcures were indicated prominently at 100° C. by shortness and low tensile, whereas at room temperatures this shortness might remain concealed.

These results were limited by the dimensions of the temperature control chamber attached to the testing machine, which permitted tests only up to 500 per cent elongation. Since then the tester has been equipped with a 48-inch tank which allows test pieces to be stretched at the desired temperature to rupture, so that complete stress-strain data and ultimate tensiles can be obtained.

Temperature Control Equipment

Figure 1 shows the Scott tester with the new temperature control tank attached. The rectangular tank has interior dimensions of about 7 (front) × 6 (side) × about 48 inches, and is equipped on the bottom with an ordinary packing gland through which a smooth round brass extension of the stretching rod slides without leakage when the tank is full of water or other liquid.

Externally the tank is equipped front and back with long, wire-glass windows which permit elongation measurements to be made in the usual way; a hinged porthole door is located on the front at the bottom for cleaning purposes and the removal of broken test pieces. Internally the tank is divided longitudinally into three parallel sections by means of two perforated metal plates fitted into grooves, one on each side of the stretching rod. In the right-hand compartment a long stirring rod having two sets of small blades, operated by a small motor and worm gear mounted on the top of the tank, helps to keep uniform the temperature of the liquid in the tank. These compartments can be packed with cracked ice when testing at 0° C. is undertaken, the perforated plates preventing the ice from obscuring the descent of the stretching rod and the reading of elongation measurements.

Two electric immersion heaters at the bottom of the tank keep the liquid at the temperature desired. For temperatures up to 100° C. water is the best liquid; for temperatures above 100° C. glycerol, on account of its negligible action on rubber, has proved to be a convenient medium.

Tests on Commercial Inner Tubes

Practically no data have been published on the physical properties of commercial rubber articles at high temperatures. It is well known that automobile tires and tubes are frequently subjected to extreme temperature variations. Small passenger tires may reach 70° to 100° C. in hot weather,

while large bus-truck tires frequently reach and remain at vulcanizing temperatures for considerable periods.

Blow-outs occur most commonly in hot weather and are attributed either to tires being worn too far into the carcass or to mechanical defects of construction if the tire is relatively unworn. It is generally understood that the rubber in a tire carcass serves to insulate the fabric cords and plies from one another, as well as to bond these into a flexible, solid mass. If at higher temperatures the rubber becomes short and weak, it is probable that the insulating function of the rubber may gradually be destroyed by constant flexing, thus allowing a separation to start that may ultimately result in a blow-out. It seems therefore that for products of this sort tensile tests of compounds made at room temperatures are more or less meaningless as far as tire performance is concerned. On the other hand, if the compounds are tested at high temperatures and found to be reasonably strong and firm, particularly after aging, it may be assumed that, when the tire becomes hot, the rubber in the carcass will continue to perform satisfactorily its proper function during service.

Somewhat similar considerations apply to tubes; the main difference is that the tube is supported and kept from rupture by its confinement. Hence a tube that has softened from excessive heat will sometimes continue to perform its office of holding air as long as the tire is good. More frequently, however, it will thin out on softening and chafe through at some rough spot in the casing. Moreover, tubes in this condition are useless once they are removed from the tire because they cannot be reinserted without buckling. In overheated truck tires tubes sometimes practically melt and become incapable of holding air, so that a good casing may be ruined by a sudden let-down.

There is an element of human risk involved in the use of tires and tubes which should render the study of their behavior at high temperatures a matter of considerable importance. The actual testing of the strength of tires at higher temperatures in the laboratory is difficult and thus far has been best approached through friction-stripping tests. Somerville and Cope (*5*) have already reported in similar tests on belting that the friction pull at 100° C. was about half of that found at 0°. Tubes, on the other hand, are easy to test because they are of suitable thickness and can be readily cut into the ordinary dumb-bell test pieces of the proper shape and dimensions.

The fact that tubes are exposed to oxidizing conditions as well as heat adds importance to the study of aging in relation to high-temperature testing.

In order to study the behavior of inner tubes under a fairly wide spread of temperature conditions, this laboratory recently purchased on the open market passenger car inner tubes of practically all the available makes. These tubes

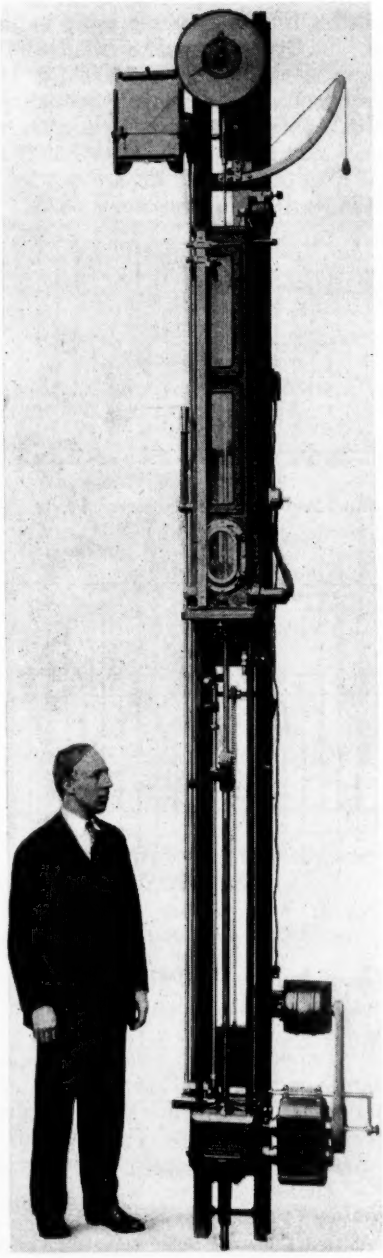

FIGURE 1. SCOTT TESTER WITH TEMPERATURE CONTROL EQUIPMENT

were subjected to tests at 0°, 25°, 70°, and 100° C., covering tensile properties before and after aging in the air bomb, oxygen bomb, and Geer oven, tear resistance before and after aging, and permanent set at 0° and 100° C. In view of the large number of tubes tested, it was found impossible to give all the results here, so that only those pertaining to large-sized passenger car tubes (6.50 × 17 to 7.50 × 17 inches) are shown. The data obtained at 70° are omitted so as not to complicate the graphs with too many points. The results

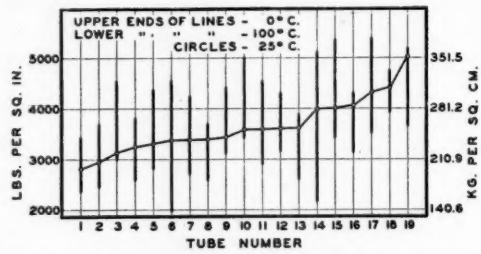

FIGURE 2. TENSILE STRENGTH OF LARGE PASSENGER TUBES

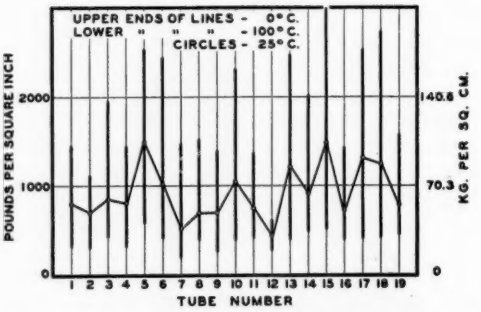
UPPER ENDS OF LINES - 0° C.
LOWER " " " - 100° C.
CIRCLES - 25° C.
POUNDS PER SQUARE INCH
2000
1000
0
140.6
70.3
0
KG. PER SQ. CM.
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19
TUBE NUMBER

FIGURE 3. MODULUS AT 500 PER CENT OF LARGE PASSENGER TUBES

are given in graphical form and without identification. Each tube has a number, and any manufacturer desiring to identify his own tube will be so advised upon request.

TENSILE STRENGTH. Figure 2 shows the tensile strength of nineteen large-sized passenger car tubes at 0°, 25°, and 100° C. The length of each vertical line shows the drop in tensile strength between 0° and 100°. The tubes are arranged in the order of ascending 25° tensile, and the line interconnecting the 25° circles merely serves to emphasize the change in tensile from one tube to another.

It is evident that there are large variations in tensile spread between 0° and 100°, the greatest loss being about 58 per cent of the tensile at 0° (tube 14), and the smallest about 18 per cent (tube 18); also, that high tensile at room temperature

or at 0° does not necessarily mean high tensile at 100°. A few of the tubes show at 100° only a slight drop in tensile from that at room temperature, while many of them show a large drop. This chart shows that it is not possible to judge from the tensile strength at room temperature how a tube will behave at higher temperatures. But it is clear that, in

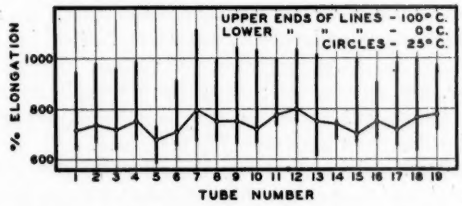

FIGURE 4. ULTIMATE ELONGATION OF LARGE PASSENGER TUBES

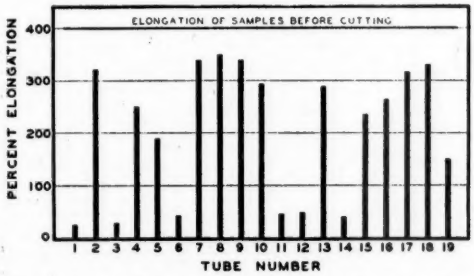

FIGURE 5. PERMANENT SET OF LARGE PASSENGER TUBES AT 0° C.

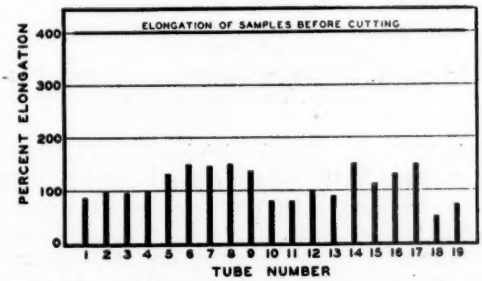

FIGURE 6. PERMANENT SET OF LARGE PASSENGER TUBES AT 100° C.

general, a tube or tire becomes stronger in cold weather and weakens in hot weather.

An ideal vulcanized product might conceivably be one which would show practically no tensile change between 0° and 100°. While it is doubtful that such a condition is actually attainable, it is apparently possible to come within reasonable approximation of it, as shown by tube 18; and it

is entirely possible to vulcanize rubber so that the 25° and 100° tensile curves are identical, as will be shown later.

The composition of the tubes being, in most cases, unknown, it is difficult to draw satisfactory conclusions regarding the relation between the results obtained and the state of vulcanization. If a large drop in tensile from room temperature to 100° is taken to indicate overcure, it would seem that this should be reflected in low permanent set at 0°. In a general way this is true; for instance, tubes 6 and 14, which show the greatest tensile drops, have low set values. Tubes 1 and 2, however, are noteworthy; both have practically the same tensile change, yet 1 shows a very small set (25 per cent) at 0°, while 2 shows a high one (320 per cent).

Modulus. Figure 3 shows the effect of temperature on the modulus of the tubes; the stresses at 500 per cent elongation, measured at 0°, 25°, and 100°, are plotted as were the

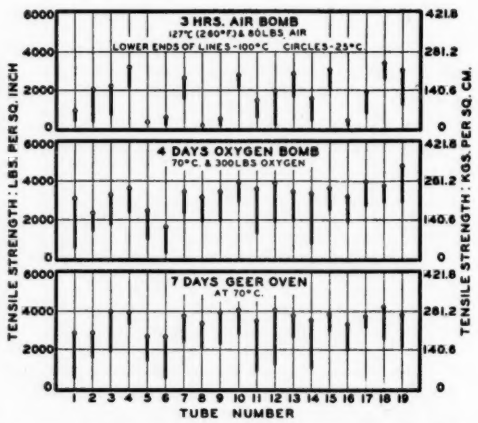

Figure 7. Tensile Strength of Large Passenger Tubes after Aging

tensiles in Figure 2. The line joining the 25° values is quite erratic, whereas in the tensile curve it gradually ascended. There is no relationship between modulus and tensile changes at different temperatures. Tube 18, which had the smallest tensile change, shows the second largest modulus change; tube 12, which has the smallest modulus change, did not show the smallest tensile change.

Ultimate Elongation. The values obtained for ultimate elongation appear in Figure 4. Here there is less variation from tube to tube than was seen in tensile and modulus. The higher values were obtained at 100°; hence, the relation of elongation to temperature change is the reverse of that of tensile and modulus. The line joining the 25° elongation values is to some degree a reversal of the line joining the modulus values, peaks in the one corresponding to dips in the

other. In a general way both modulus and elongation values at 0° and 100° follow those at 25°, but with greater fluctuations.

PERMANENT SET AT 0° C. Permanent set values obtained at 0° are shown in Figure 5. The specimens were stretched 400 per cent, held 16 hours at room temperature, immersed one hour in ice water, cut, and measured in the ice water after 5 minutes. The percentage increase in length over the origi-

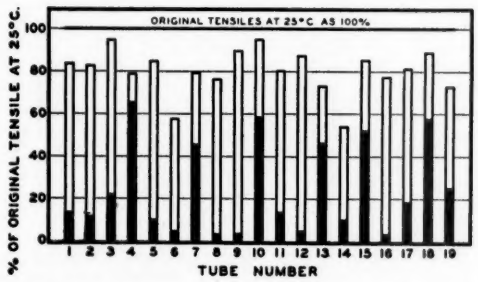

FIGURE 8. TENSILE STRENGTH OF LARGE PASSENGER TUBES AT 100° C. BEFORE AND AFTER AGING

Column height, original tensile; shaded height, tensile after aging 3 hours in air bomb at 127° C. (260° F.) and 80 pounds air pressure.

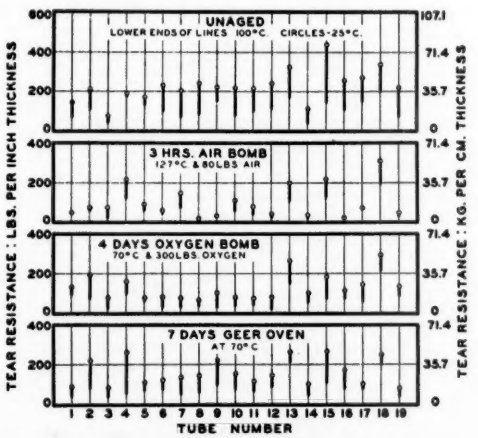

FIGURE 9. TEAR TESTS ON LARGE PASSENGER TUBES

nal was taken as the permanent set at 0°. The set values are for the most part either small or large. The small ones are in the minority and probably indicate a "tight" cure. It is noteworthy that nearly two-thirds of the tubes have high set values at 0°, which may be taken as an indication either of a soft cure or of the use of very low sulfur by some manufac-

turers. Apparently high permanent set at low temperatures is not considered a detrimental condition in inner tubes. It is impossible to correlate the set values with the tensile, modulus, or ultimate elongation values at 100°.

PERMANENT SET AT 100° C. Set values found at 100° are shown in Figure 6. The specimens, stretched 400 per cent,

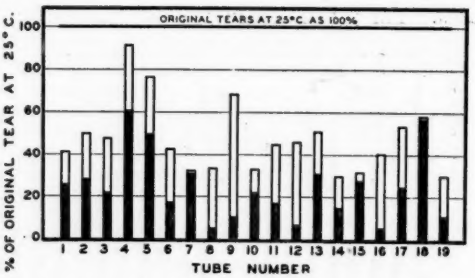

FIGURE 10. TEAR RESISTANCE OF LARGE PASSENGER TUBES AT 100° C. BEFORE AND AFTER AGING

Column height, original tear; shaded height, tear after aging 3 hours in air bomb at 127° C. (260° F.) and 80 pounds air pressure.

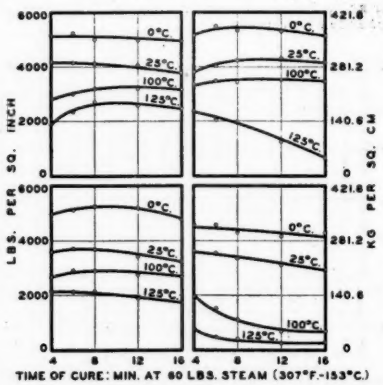

FIGURE 11. TENSILE STRENGTH OF TWO TYPES OF TRUCK TUBE STOCK BEFORE AND AFTER AGING

Right, type 1; left, type 2.
Above, unaged; below, aged 3 hours in air bomb at 127° C. (260° F.) and 80 pounds air pressure.

were boiled in water for 24 hours, cut, and measured in the boiling water after 5 minutes. The percentage increase in length over the original was taken as the set. The differences from tube to tube are much smaller than those at 0°, but there is no definite relation between the two series.

TENSILE AFTER AGING. Figure 7 shows the effect of aging in the air bomb, oxygen bomb, and Geer oven on the tensiles

at 25° and 100°. In Figure 8 the tensiles at 100°, before and after aging in the air bomb, are shown as percentages of the original tensile at 25°. A few of the tubes resist the air bomb treatment outstandingly well and show fairly good 100° tensiles after aging. Most of them are badly damaged. It seems clear, therefore, that many inner tubes, after having been in service for some time, probably do not have much strength in a hot tire.

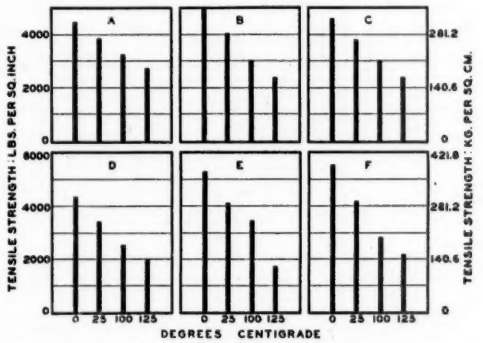

FIGURE 12. TENSILE STRENGTH OF TRUCK TUBE STOCKS

Average of five cures.

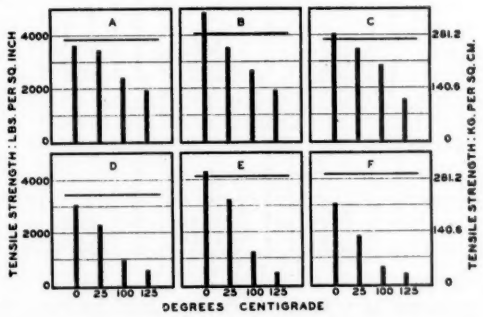

FIGURE 13. TENSILE STRENGTH OF TRUCK TUBE STOCKS AFTER 3 HOURS IN AIR BOMB AT 127° C. AND 80 POUNDS AIR PRESSURE

Horizontal lines, original tensile at 25° C.; average of five cures.

TEAR RESISTANCE. The tear test data shown in Figure 9 were obtained by the Crescent method. Tear resistance is of particular interest in inner tubes. It has no direct relation to tensile strength but, like the latter, is dependent on the degree and kind of loading, and state of cure; it also diminishes at higher temperatures. The results show tear resistance at 25° and 100°, before and after aging. The majority

of the tubes are severely damaged by the aging periods, but one of them, 18, stands out from the others in that it is good at both testing temperatures in all the tests. Figure 10 shows the tear resistance at both temperatures, after air bomb aging, as percentages of the original tear at 25°.

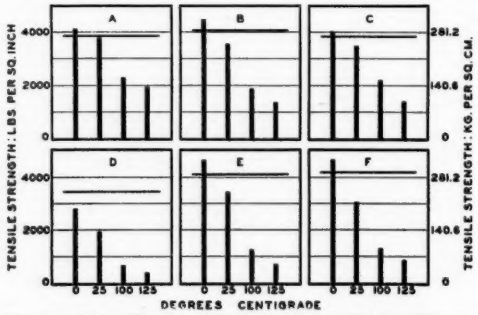

FIGURE 14. TENSILE STRENGTH OF TRUCK TUBE STOCKS AFTER 4 DAYS IN OXYGEN BOMB AT 70° C. AND 300 POUNDS OXYGEN PRESSURE

Horizontal lines, original tensile at 25° C.; average of five cures.

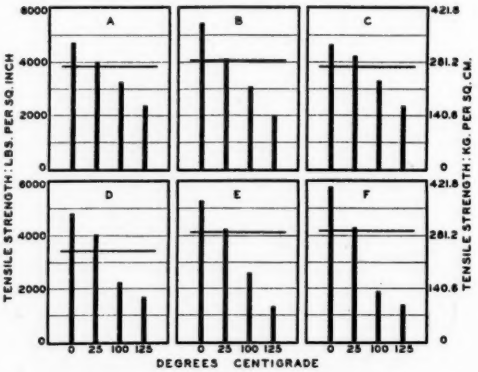

FIGURE 15. TENSILE OF TRUCK TUBE STOCKS AFTER 7 DAYS IN GEER OVEN AT 70° C.

Horizontal lines, original tensile at 25° C.; average of five cures.

UNCURED BUS-TRUCK TUBE STOCKS

Owing to the difficulty of cutting uniform specimens from large bus-truck tubes, it was arranged, through the kindness of about fifteen manufacturers, to have uncured stocks placed at the authors' disposal. A range of cures was made on each sample in a laboratory press, and the flat slabs were tested instead of finished tubes. This work was so voluminous that it was found impossible to reproduce it all here; data on only six compounds are given.

Figure 11 shows the behavior of a range of cures on two different types of truck tube stock when tested at 0°, 25°, 100°, and 125°, before and after air-bomb aging. Both compounds are reasonably comparable in behavior at different temperatures when tested before aging. However, after aging, one of them stands up much better at 100° and 125° than the other. The former would naturally be expected to perform better than the latter in severe service.

Figures 12 to 15 show tensile strength of six different compounds at 0°, 25°, 100°, and 125° before and after aging in the air bomb, oxygen bomb, and Geer oven, respectively. The average tensiles of the 4-, 6-, 8-, 12-, and 16-minute cures at 60 pounds steam (153° C.) were used in constructing the graphs. Compounds *A*, *B*, and *C* have distinctly better properties at the high temperatures, both before and after aging, than *D*, *E*, and *F*. There was found to be pronounced variation in the properties of the different truck tube stocks,

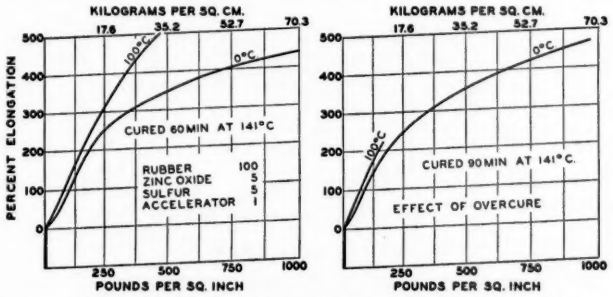

FIGURE 16. EFFECT OF OVERCURE ON STRESS-STRAIN CURVE OF A HIGH SULFUR STOCK AT 100° C.

more especially at the higher temperatures and after aging. The stocks shown here were therefore selected so that the extremes would be represented. *A*, *B*, and *C* may be taken as representative of the best under the conditions of test, while *D*, *E*, and *F* belong to the class which showed poor results.

Since the formulas of these tube stocks are unknown to the writers, it is impossible to correlate the results obtained with their composition. Assuming the tests described to mean something, the results indicate that some types of bus-truck tube stocks are better suited than others to the type of service for which they are intended; further, that the heat- and age-resistance of some of them could be improved. A suggestion as to one means of effecting such improvement is given at the end of the paper.

DEVELOPMENT WORK ON HEAT-RESISTING STOCKS

The results reported in 1928 (*5*) showed how two different cures of the same stock could behave quite differently on stressing at 100°, while at 0° they showed little difference.

Figure 16 is a chart used in 1928 to illustrate this point; it shows the breaking short of an overcure on stressing at 100°, a condition which does not appear in the 0° curve.

The results shown in Figure 16 relate to two isolated cures of a certain stock. It should be interesting to see how the same compound used in 1928 behaves over a wide range of cures. The accelerator used in the mix was diphenylguanidine (D. P. G.) and Figure 17 shows tensile-time curves at 25° and 100° for the same D. P. G. compound. If judged by the 25° curve, the stock might readily be accepted as a good one. The 100° curve, however, proves definitely that the 30-minute cure is the only one not badly overcured. Such a stock is clearly unsuitable for anything that may be exposed to high temperatures in service. There was no need to age it.

D. P. G. is not the only accelerator that may cause this decline at 100° if too much sulfur is present; any or every accelerator will behave in the same way. Figure 18 shows tensile-time curves, before and after aging, for a mercapto-

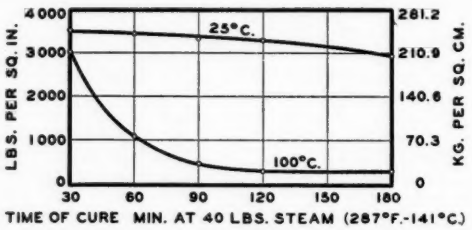

FIGURE 17. TENSILE STRENGTH OF HIGH SULFUR–D. P. G. STOCK

Rubber	100	Zinc oxide	5
D. P. G.	1	Sulfur	5

benzothiazole (Captax) stock containing an excessive amount of sulfur—namely, 4 per cent on the rubber. Before aging, the 25° tensile curve again indicates the stock to be good, whereas the 100° curve proves it to be overcured above the 90-minute cure.

The results obtained after aging the stock in the oxygen bomb are characteristic and significant. If the aged stock is judged by the tensile results at 25°, it appears to be a fairly good aging compound; the 30-minute cure is even slightly improved, which is characteristic of undercures. When tested at 100°, however, the compound has practically no tensile in any of the cures. It is completely brittle and worthless. Testing at 100° after aging, therefore, may reveal precarious conditions of deterioration, which are not noticeable in tests made at 25°.

Similar but far less pronounced effects are seen in Figure 19, which gives the results obtained on a normal sulfur–Captax stock, before and after aging. The unaged stock evidently stands up well at 100°, for the 100° tensile curve is close and

nearly parallel to the 25° curve and shows no break like that in Figure 18. Also, the aged stock, tested at 25°, should rightly be considered excellent. There is no doubt of the excellence of this stock, for it has been proved by years of successful commercial use. Nevertheless, the 100° tests made on the aged stock reveal a definite injury that is scarcely noticeable in the 25° tests and even indicate approximately at what curing time the rubber begins to overcure.

These results show that it is possible to make stocks with the normal amount of sulfur, that will maintain, over a wide

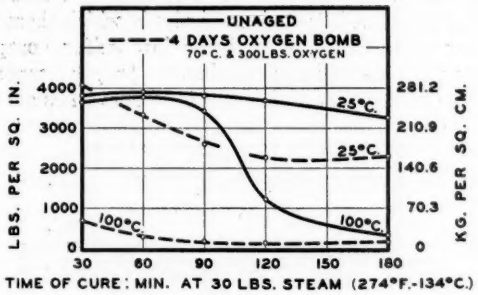

FIGURE 18. TENSILE STRENGTH OF HIGH SULFUR–CAPTAX STOCK BEFORE AND AFTER AGING

Rubber	100	Zinc oxide	10
Stearic acid	1	Captax	1
Agerite powder (phenyl-β-naphthylamine)	1	Sulfur	4

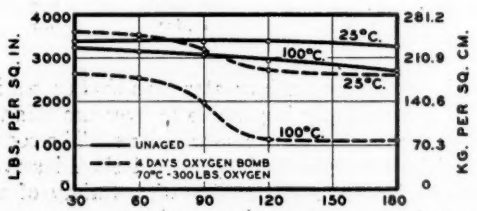

FIGURE 19. TENSILE STRENGTH OF NORMAL SULFUR–CAPTAX STOCK BEFORE AND AFTER AGING

Rubber	100	Zinc oxide	10
Stearic acid	1	Captax	1
Agerite powder	1	Sulfur	2.5

range of cures, fairly good tensile strength at 100°. It has been found during the work that the type of acceleration has an important bearing on the results; that is, when the sulfur ratio is kept constant, some accelerators may cause severe overcuring while others do not. Captax is one of those that have the least tendency to cause overcuring.

The sulfur ratio has been found to be of supreme importance. If it is desired to compound stocks that will show high tensile strength at 100° after aging as well as before, it is

necessary to go to much lower sulfur ratios than 2.5 per cent.

Figure 20 shows the results obtained on a stock cured with 0.5 per cent of sulfur on the rubber, the acceleration consisting of Captax assisted by Tuads (tetramethylthiuram disulfide) in the proportions indicated. This compound is unique in that the tensile curves of the unaged stock at 25° and 100° and the tensile curves of the stock aged in the oxygen bomb, at 25° and 100°, almost coincide over the entire range of cures from 30 to 180 minutes. As a matter of fact, the unaged 100° curve lies slightly above the 25° curve. This reversal of the order shown in Figures 17 to 19 is not due to experimental error but is the natural order in which these curves appear for a great many of these low sulfur compounds when properly balanced and cured at the proper temperature. In fact, the amount by which the 100° curve lies above the

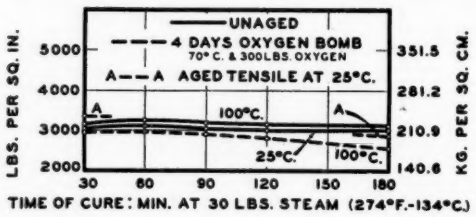

FIGURE 20. TENSILE STRENGTH OF LOW SULFUR, HEAT-RESISTANT STOCK BEFORE AND AFTER AGING

Rubber	100	Captax	1
Stearic acid	1	Tuads	0.2
Agerite powder	1	Sulfur	0.5
Zinc oxide	10		

25° curve is frequently much greater than that shown in Figure 20. It is apparently impossible to overcure this type of stock under any ordinary curing conditions. The compound is very resistant to heat and aging and should serve as a suitable basis for the compounding of a variety of articles that are required to withstand severe heat.

LITERATURE CITED

(1) Breuil, P., *Caoutchouc & gutta-percha*, 7, 4073 (1910).
(2) Le Blanc, M., and Kroeger, M., *Kolloid-Z.*, 37, 205–14 (1926).
(3) Rossem, A. van, and Meijden, H. van der, *J. Soc. Chem. Ind.*, 45, 67–72T (1926).
(4) Rossem, A. van, and Meijden, H. van der, *Kautschuk*, 1927, 364–71.
(5) Somerville, A. A., and Cope, W. H., *India Rubber World*, 79, 64–71 (1928).
(6) Tener, R. F., Kingsbury, S. S., and Holt, W. L., Bur. of Standards, *Tech. Paper* 364 (1928).

[Reprinted from Industrial and Engineering Chemistry, Vol. 25, Pages 1151–1152, October, 1933.]

Mechanism of Rubber Aging

BERNARD L. JOHNSON AND FRANK K. CAMERON
University of North Carolina, Chapel Hill, N. C.

The position of the diffraction lines obtained on x-ray photographs of rubber does not change upon aging the rubber in the oven at 70° C. for 10 days. However, the intensity of the lines decreases as the aging time is increased. The increased elongation needed to produce fibering in aged rubber is considered necessary to expel the increased concentration of lower polymers, introduced by depolymerization during aging, from the crystalline aggregates or fibers allowing the latter to diffract the x-rays. Oxidation might also produce the same effect by the formation of obstacles to the stretching out of tangled molecules or micelles. The rate of depolymerization upon aging vulcanized rubber in the oven at 70° C. is studied, and a curve of the elongation at which the crystalline modification first appears is plotted against the time of aging. The same general curve is obtained for rubber both with and without phenyl-β-naphthylamine, indicating that an antioxidant such as phenyl-β-naphthylamine does not affect the rate of depolymerization of rubber or the elongation necessary to produce fibering in aged rubber.

AMONG the present theories of the aging of rubber are two which are closely related to the fundamental structural characteristics of rubber. This investigation was made to determine to what degree those structural changes might be responsible for the aging of rubber.

One theory is that the deterioration of rubber is due to its unsaturation of carbon, oxidation taking place at the double bond. Weber (*5*) has given two facts in support of this

theory: (1) If vulcanized rubber is exposed to sunlight in atmospheres of hydrogen, carbon dioxide, air, oxygen, and in vacuum, respectively, only the samples in air and oxygen deteriorate in a period of several months. (2) It is known that oxygen carriers, such as copper and manganese, have a severe deteriorating action on rubber. Two inconsistencies in the oxidation theory listed by the same writer are that vulcanized rubber, having a lower degree of unsaturation, is more susceptible to deterioration than crude rubber of a higher degree of unsaturation, and that over- or undervulcanized rubber deteriorates with increased activity in comparison to properly cured rubber.

A second theory (to be discussed in this paper) is that the unstable balance of polymers in the rubber might cause its deterioration. Evidence of the depolymerization of rubber on artificial aging is given in the work of Bary and Fleurent (*2*) who found that the more polymerized part, β-rubber, decreased on oven-aging. The increase in the benzene-soluble α-rubber with increase of aging temperature is shown in the following table given by Bary and Fleurent:

Aging Conditions		Solubility in Benzene
Hours	° *C.*	%
75	52	30.1
75	63	49.3

The x-ray behavior of rubber may also indicate this depolymerization. Hauser and Mark (*4*) have shown that with crude rubber the x-ray interferences appear only at an elongation of 80 to 100 per cent. They also proved that these interferences do not change position from the moment of their appearance to an elongation of 1000 per cent, but that their intensity increases proportionally to the elongation. Bary and Hauser (*3*) have explained the formation of x-ray patterns upon the elongation of rubber on the basis that in the unstretched rubber, crystalline aggregates or fibers exist but are swollen by the lower polymers so that it is impossible for them to give a diffraction pattern. When rubber is rapidly stretched, the lower polymers (α-rubber) are expelled, leaving the regularly oriented crystalline aggregates (β-rubber) which produce the x-ray pattern. From this view the fact (as shown later) that, as the time of oven-aging is increased, the elongation necessary for a pattern must be increased, may be interpreted as meaning that there had been a depolymerization into the alpha form and the greater elongation was required to produce the crystalline units or fibering because the concentration of the lower polymers to be expelled had been increased by that depolymerization during aging. Although the above explanation is plausible because we know that depolymerization takes place during oven-aging, it is not the only one which might be advanced. For instance, if fibering is considered as a stretching out of tangled molecules or

micelles (*1*), then oxidation alone might produce obstacles to the production of fibers.

Type of Rubber

A specially compounded rubber was prepared in order that it be as transparent as possible and not contain fillers which would produce diffraction lines on the film which might be confused with those arising from the rubber. Two batches

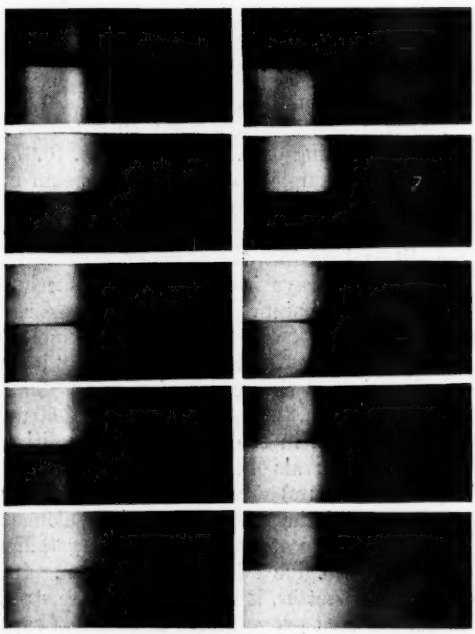

FIGURE 1. DECREASE IN INTENSITY OF DIFFRACTION PATTERNS WITH INCREASE IN AGING TIME

of stock were mixed which had the following composition by weight, except that the antioxidant was left out of one batch:

Pale crepe	1000
Sulfur	20
Zinc oxide	10
Stearic acid	25
Accelerator (tetramethylthiuram monosulfide)	2.5
Antioxidant (phenyl-β-naphthylamine)	7.5

This stock was cured into slabs 2 mm. thick. The aging properties of these two stocks were determined by tensile strength tests after aging in the oven at 70° C. These results are as follows:

Aging Period	With Antioxidant	Without Antioxidant
Days	*Pounds per square inch*	
Unaged	3660	3470
4	3780	3580
7	3680	3130

Since these data show a distinct difference in behavior of the two stocks after oven-aging, it was decided to obtain x-ray photographs of the two types of rubber in an attempt to determine whether depolymerization or some change in the rubber molecule or micelle was responsible for the more rapid rate of deterioration of the stock without antioxidant.

X-Ray Procedure

The diffraction patterns were obtained on a General Electric diffraction apparatus having a Coolidge tube with a molybdenum target operating at 30,000 volts potential. The regular set-up for examining a powdered crystal was used, the rubber sample replacing the tube containing the powdered crystal. The radiation from the x-ray tube passed through a slit having an opening of 0.18 × 12.7 mm. (0.07 × 0.50 inch). The rubber sample was held in the beam of x-rays passing through the slit by clamps fastened at the sides of the cassette which is a quadrant-shaped metal case fitting around the slit and against the cylinder housing the x-ray tube. The diffracted rays from the rubber specimen were filtered through a zirconium filter and then recorded on a photographic film 4.76 × 40.6 cm. ($1^7/_8$ × 16 inches) which was placed in the form of an arc of 20.3 cm. (8 inches), the rubber sample being at the center of the arc. The rubber was cut into strips 2 mm. thick, 5 mm. wide, and 60 mm. long. These strips were aged in the unstretched condition in the oven at 70° C. for intervals of time to 10 days. After resting overnight (about 15 hours) at room temperature, x-ray photographs were taken of the rubber at various elongations to determine the elongation at which sufficient crystalline modification was present to give a diffraction pattern. In placing the rubber in the cassettes, it was in every case stretched at the rate of 100 per cent per second. The time of exposure to the x-rays was 6 hours.

Discussion of Results

Figure 1 illustrates the decrease in intensity of the diffraction patterns as the aging time is increased. The photographs in Figure 1 were in every case taken at a constant elongation of 500 per cent. There is a gradual decrease in intensity of the diffraction lines at 2- and 4-day aging; the last diffraction lines are obtained at 6 days. The amorphous band only is obtained at 7 days of aging. This disappearance of the first line at 6.5 Å., which represents the greatest interplanar spacing obtained for rubber with x-rays of 0.712 Å. in wave length, was taken as the last of the crystalline pattern. The position of the diffraction lines did not change upon 10-day aging of the rubber.

In Figure 2 the crosses represent crystalline patterns and the circles, amorphous patterns for each of the elongations indicated on the ordinate. Each point represents a photo-

graph as shown in Figure 1, and each photograph was obtained by stretching a separate rubber sample to the indicated elongation. The time of oven-aging at 70° C. is given in days on the abscissa. Upon drawing a curve through the first amorphous points for each elongation and another curve through the last crystalline points, the shaded area of transition from the alpha to the beta modification is bounded. Upon aging the rubber, the elongation necessary to produce a pattern rises rapidly for the first day, after which it proceeds along a straight line. The width of the sample of rubber was doubled and other changes were made in an attempt to obtain points beyond 10 days, but the curve could not be continued beyond 10 days because after aging for 10 days the rubber broke under the 625 per cent elongation which was necessary to produce the diffraction lines. At no time was an amorphous pattern obtained with the antioxidant-free rubber at an elongation for which a crystalline pattern had

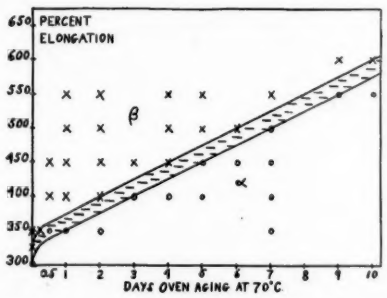

FIGURE 2. ELONGATION AT WHICH THE CRYSTALLINE MODIFICATION FIRST APPEARS *vs.* TIME OF AGING

been obtained for the rubber containing antioxidant, so the same curve will apply to both types of rubber. The portion below the curve is represented as α-rubber and that above the curve as β-rubber. It is significant that the rate of formation of these lower polymers, as indicated by the increase in elongation necessary for fibering, is the same for both the rubber containing antioxidant and that without antioxidant as it indicates that depolymerization is not the major factor in deterioration of rubber and that the presence of phenyl-β-naphthylamine does not change the fibering of rubber although it greatly prevents its deterioration upon aging.

ACKNOWLEDGMENT

The authors wish to acknowledge their indebtedness to N. A. Shepard and J. N. Street of the Firestone Tire and Rubber Company for the preparation of the rubber stock, and to L. W. Joyce, president of the Southern Webbing Mills, Inc., who made this investigation possible.

Literature Cited

(1) Acken, Singer, and Davy, Ind. Eng. Chem., 24, 54 (1932).
(2) Bary and Fleurent, *Compt. rend.*, 184, 947 (1927).
(3) Bary and Hauser, *Rubber Chem. Tech.*, 1, 401 (1928).
(4) Hauser and Mark, *Kolloidchem. Beihefte*, 23, 64 (1926).
(5) Weber, L. E., Ind. Eng. Chem., 18, 963 (1926).

[Reprinted from Industrial and Engineering Chemistry, Vol. 25, Pages, 1219–1223, November, 1933.]

Effect of Oils and Chemicals on DuPrene Compounds

O. M. HAYDEN AND E. H. KRISMANN

E. I. du Pont de Nemours & Company, Wilmington, Del.

A typical oil-resisting natural-rubber stock is compared with a DuPrene compound containing the same fillers in the same volume relationship. Both compounds are immersed in various animal, vegetable, and mineral oils, and synthetic organic solvents which swell rubber for periods ranging from a few hours to several weeks. The effect of immersing a pure gum DuPrene compound in kerosene for two years is also shown. The aromatic hydrocarbons and chlorinated compounds affect DuPrene and rubber about equally, but practically all of the other swelling agents have much less effect on DuPrene than on rubber, the greatest differences being shown by tests conducted at elevated temperatures. The effect of hot and cold acids and alkalies is reported in terms of reduction in tensile strength during immersion.

DUPRENE is the trade name for a synthetic rubber obtained by the polymerization of chloroprene, which was first described by Carothers, Williams, Collins, and Kirby.[1] These authors described the synthesis of chloroprene, the conditions of polymerization and the properties of chloroprene polymers, pointing out particularly that this synthetic rubber is much more resistant than natural rubber to most chemicals, especially oils and solvents. The purpose of this paper is to present further data with reference to the effect of various oils and chemicals on DuPrene compounds.

[1] *J. Am. Chem. Soc.*, 53, 4203 (1931).

Unvulcanized DuPrene is a plastic material somewhat similar to crude rubber. When masticated on a rubber mill it becomes quite plastic and may then be compounded with vulcanizing agents, reënforcing pigments, coloring ingredients, softeners, fillers, etc.

DuPrene compounds that contain, in addition to DuPrene, only such added ingredients as are essential for vulcanization have physical properties similar to pure gum rubber; but for most commercial purposes DuPrene is compounded with a large proportion of fillers and other ingredients, the nature and amount of the added ingredients being dependent upon the conditions of service to which the article is to be subjected. Consequently, one cannot speak of the oil resistance or any other property of DuPrene except in the most general terms. Specific information must always relate to a certain DuPrene compound vulcanized under certain conditions. Likewise, if one wishes to compare the oil resistance or other properties of a particular DuPrene compound with rubber, the rubber compound must be described in equal detail; otherwise the comparison will be of no value.

The formula for a typical oil-resisting natural rubber stock and for a comparable DuPrene compound containing the same fillers in the same volume relationship is as follows:

	Compound R-1	Compound D-1		Compound R-1	Compound D-1
DuPrene	...	100	Cottonseed oil	1	2
Smoked sheets	100	..	Stearic acid	1	...
Soft whiting (40 vol.)	112	85	Wood rosin	.	5
Gastex[a] (20 vol.)	38	28.5	Neozone D (phenyl-β-naphthylamine)	2	2
Glue (10 vol.)	15	11.5	Sulfur	6	1.5
Zinc oxide	10	10	Du Pont Accelerator 808 (butyraldehyde aniline)	1	...
Light calcined magnesia	...	10			

[a] Trade name for a special variety of carbon black.

Table I shows the physical properties of these two compounds over a wide range of cures. The DuPrene stock has higher tensile strength, much higher elongation, better tear resistance, about six points lower hardness at all cures, and a more rubbery feel than the corresponding natural rubber stock. It is characteristic of DuPrene that it will take up considerably larger volumes of pigment than rubber without becoming stiff and boardy. DuPrene compounds have higher elongation than similarly compounded natural rubber stocks, and they maintain desirable physical properties over a much wider range of cure.

Effect of Kerosene

Table II shows the effect of immersing these two compounds, cured 15, 30, 45, and 60 minutes at 287° F. (141.7° C.) in kerosene at room temperature and at 212° F. (100° C.).

All swelling tests reported were conducted on molded samples 1 × 2 × 0.080 inch thick. Samples were weighed before immersion and, after removal from the solution, were

TABLE I. PHYSICAL TESTS ON COMPOUNDS D-1 AND R-1

Cure at 287° F. (141.7° C.)	D-1 (DuPrene)						R-1 (Rubber)					
	200% modulus		Tensile		Elongation		200% modulus		Tensile		Elongation	
Min.	*Lb./ sq. in.*	*(Kg./ sq. cm.)*	*Lb./ sq. in.*	*(Kg./ sq. cm.)*	%		*Lb./ sq. in.*	*(Kg./ sq. cm.)*	*Lb./ sq. in.*	*(Kg./ sq. cm.)*	%	
3	No cure		...	...	...		375	(26.4)	1350	(94.9)	470	
5	225	(15.8)	1225	(86.1)	550		575	(40.4)	1650	(116.0)	420	
7	325	(22.8)	1525	(107.2)	560		650	(45.7)	1600	(112.5)	400	
10	375	(26.4)	1600	(112.5)	530		700	(49.2)	1650	(116.0)	380	
15	500	(35.1)	1725	(121.2)	510		800	(56.2)	1550	(109.0)	330	
30	625	(43.9)	1750	(123.0)	430		950	(66.8)	1325	(93.1)	260	
45	650	(45.7)	1750	(123.0)	420		950	(66.8)	1275	(89.6)	260	
60	725	(51.0)	1775	(124.8)	420		950	(66.8)	1275	(89.6)	260	

immediately wiped dry with absorbent paper and weighed within a minute or two. The percentage increase in weight was determined and percentage increase in volume calculated according to the formula:

$$\% \text{ increase in vol.} = \frac{\% \text{ increase in weight} \times \text{sp. gr. of sample}}{\text{sp. gr. of swelling medium}}$$

The data of Table II indicate that the swelling effect of kerosene on the DuPrene compound at room temperatures is independent of the state of cure within the range tested. However, the 15-minute cure on the rubber compound swells more than the longer cures. At 212° F. the 45- and 60-minute cures of both the DuPrene and the rubber compound swell less than the shorter cures.

TABLE II. EFFECT OF KEROSENE ON COMPOUNDS D-1 AND R-1

Cure at 287° F. (141.7° C.)	Compound	Increase in Vol. at 82° F. (28° C.)			Increase in Volume at 212° F. (100° C.)				
		24 hours	3 days	7 days	3.5 hours	24 hours	4 days	6 days	8 days
Min.		%	%	%	%	%	%	%	%
15	D-1	15.2	22.0	22.0	36.2	41.7	42.0	40.7	43.1
	R-1	80.8	83.6	83.6	107.2	167	317.0	Disintegrated	
30	D-1	15.6	23.8	23.8	31.9	40.4	40.4	39.0	39.4
	R-1	71.4	74.5	74.5	100.2	153.0	270.0	Disintegrated	
45	D-1	14.2	22.8	22.8	32.1	36.2	35.8	36.5	37.8
	R-1	73.5	77.9	77.9	95.3	142.3	254.0	Disintegrated	
60	D-1	16.8	22.0	22.0	30.6	37.0	36.7	37.0	37.2
	R-1	76.7	78.8	78.8	94.2	144.0	254.0	350.0	Disintegrated

The most striking difference between the two compounds in this test is not the fact that the DuPrene compound swells only about 30 per cent as much as the rubber compound in cold kerosene and about 15 per cent as much as the rubber compound in hot kerosene, but that the rubber compound becomes very tender and in hot kerosene it completely disintegrates and goes into solution, whereas the DuPrene compound retains a large portion of its original strength and tear resistance even under conditions which cause the rubber compound to dissolve completely.

EFFECT OF OILS OTHER THAN PETROLEUM DERIVATIVES

Table III shows the effect of immersing compounds D-1 and R-1 in a variety of oils and solvents for 1, 3, and 7 days at 82° F. (28° C.). Samples for this test were all cured 45 minutes at 287° F. Cottonseed, linseed, and olive oils were taken as representative types of vegetable oils. In all cases the DuPrene compound swelled less than the rubber compound, and, what is more important, the physical properties of the DuPrene compound were affected hardly at all whereas the rubber compound became definitely more tender. The same is true of a typical animal oil, lard oil. Oleic acid swelled the DuPrene and the rubber compound to about the same extent, but again the DuPrene compound retained most

of its original toughness and tear resistance whereas the rubber compound became very tender. In turpentine the rubber compound showed a tendency toward sloughing off, a phenomenon which has not been observed with respect to DuPrene compounds in any of the swelling tests carried out in this laboratory.

TABLE III. EFFECT OF NONPETROLEUM SWELLING AGENTS

[At 82° F. (28° C.)]

IMMERSED IN:	COMPOUND[a]	INCREASE IN VOLUME		
		24 hours	3 days	7 days
		%	%	%
Cottonseed oil	D-1	0	1.0	2.5
	R-1	5.8	7.9	14.6
Lard oil	D-1	2.4	3.6	5.4
	R-1	5.4	7.1	12.3
Linseed oil	D-1	0.9	2.8	3.7
	R-1	2.2	3.7	6.8
Oleic acid	D-1	20.4	33.7	47.0
	R-1	15.9	29.2	56.7
Olive oil	D-1	0	0	0
	R-1	5.0	7.3	13.2
Turpentine	D-1	50	67	88
	R-1	113	116	135
Carbon tetrachloride	D-1	164	166	176
	R-1	160	165	172
Benzene	D-1	168	172	174
	R-1	113	114	122
Creosote	D-1	85.5	157	232
	R-1	42.8	67.2	81.6

[a] All cures 45 minutes at 287° F. (141.7° C.).

In carbon tetrachloride the DuPrene compound swelled as much as the rubber compound, and in benzene and creosote the DuPrene compound swelled more. However, even these aromatic solvents, which have a marked swelling effect and cause some tendering of DuPrene, do not affect the physical properties of DuPrene compounds to the same extent as they affect rubber.

These two stocks were also tested in a variety of swelling media not shown in the tables. Toluene, xylene, and solvent naphtha caused almost exactly the same amount of swelling as benzene, both in the case of the DuPrene and the rubber compound. Other chlorinated solvents such as trichloroethylene and tetrachloroethane have approximately the same effect as carbon tetrachloride. Other vegetable oils have an effect similar to that of cottonseed oil and linseed oil. Olive oil is an exception to the rule in that it causes practically no swelling of DuPrene compounds.

Swelling tests were also made at 212° F. in the oils shown in Table III together with a variety of other nonpetroleum swelling agents. Detailed results are not reported here in order to conserve space. At this high temperature, oleic acid, butter, lard, olive oil, coconut oil, turpentine, etc., all caused pronounced swelling of the DuPrene stock but in no case was there any sign of sloughing off or incipient disintegration. These same swelling agents at 212° F. caused the rubber compound to disintegrate and slough off on the surface.

Tests were likewise conducted on methyl, ethyl, butyl, and

amyl alcohols, on glycerol and ethylene glycol, castor oil and triethanolamine. These compounds are all alcohols in the sense that they contain hydroxy groups. None of these compounds has an appreciable swelling effect on either DuPrene or rubber.

Effect of Crude and Refined Petroleum

Table IV shows the effect of immersing the 45-minute cure of compounds D-1 and R-1 in various types of crude oil and refined petroleum products at room temperature. The Pennsylvania crude which consists largely of saturated aliphatic hydrocarbons caused the DuPrene stock to swell much less than the Midcontinent and Coastal crudes. The same is true of the spindle oils derived from Pennsylvania, Midcontinent, and Coastal crudes. The Midcontinent crudes are somewhat unsaturated; the Coastal crudes are still more unsaturated and composed largely of aromatic (naphthenic) hydrocarbons. This is in accordance with the general observation that DuPrene stands up best in saturated straight-chain hydrocarbons, is affected to a greater extent by unsaturated compounds, and is especially sensitive to aromatic hydrocarbons.

Table IV. Effect of Petroleum Swelling Agents

[At 82° F. (28° C.)]

Immersed in:	Compound[a]	Increase in Volume 24 hours	3 days	7 days
		%	%	%
Crude oil:				
Pennsylvania	D-1	2.2	7.0	9.6
	R-1	46.5	55.0	58.7
Midcontinent	D-1	6.3	11.2	20.2
	R-1	39.2	55.4	61.3
Gulf Coast	D-1	6.6	9.3	18.1
	R-1	15.5	31.6	54.2
Spindle oil:				
From Pa. crude	D-1	1.3	3.6	5.7
	R-1	11.1	20.2	33.4
From Midcontinent crude	D-1	4.2	5.9	9.2
	R-1	17.6	29.2	46.1
From Coastal crude	D-1	4.7	10.1	13.9
	R-1	17.0	29.6	51.7
Motor oil:				
Essolube	D-1	1.0	1.4	1.4
	R-1	4.5	6.9	11.0
Sun No. 30	D-1	1.8	2.2	3.1
	R-1	5.7	10.2	15.5
Atlantic No. 30	D-1	0.9	0.9	0.9
	R-1	4.2	6.4	10.7
Motor gasoline (Sunoco)	D-1	29.2	29.2	33.0
	R-1	84.0	84.0	88.5
Casing-head gasoline	D-1	8.9	8.9	8.9
	R-1	53.0	56.5	58.0

[a] All cures, 45 minutes at 287° F. (141.7° C.).

Essolube was chosen as one of the motor oils to be tested because the authors are informed that it consists of Midcontinent, Coastal, or other unsaturated crudes that are saturated by hydrogenation. Definite information as to the source of the crudes from which the Sunoco and Atlantic motor oils are made is lacking, but examination indicates that they consist largely of saturated hydrocarbons, presumably

from Pennsylvania crudes. It is noteworthy that the hydrogenated oil has but little effect on DuPrene, as would be expected from a saturated hydrocarbon, in spite of the fact that it is derived from crudes which experience indicates have a more harmful effect.

Tests were conducted on eight popular motor gasolines, and very little difference was found between any of them. Only Sunoco is reported here. This gasoline, in common with most other high-grade gasolines, is made by a cracking process and hence contains a large percentage of unsaturated hydrocarbons which affect DuPrene much more than the straight-chain saturated hydrocarbons in casing-head gasoline.

Table V shows the results of swelling tests at 212° F. in the same group of crude and refined petroleum products. Petrolatum was included in the 212° F. tests but the gasolines were omitted because of their volatility. The results of the 212° F. tests may be summarized by the statement that the advantage of DuPrene over rubber is much more pronounced at high than at low temperatures. The tremendous difference in the swelling of the DuPrene and the rubber compounds in the saturated motor oil (Essolube) and in petrolatum is especially noteworthy. There was no indication of disintegration or sloughing off of the DuPrene stock in any of these tests, whereas the rubber stock in all cases showed a tendency toward sloughing off during the first few days and in many cases disintegrated and completely dissolved before the test was completed.

TABLE V. EFFECT OF PETROLEUM SWELLING AGENTS

[At 212° F. (100° C.)]

IMMERSED IN:	COMPOUND[a]	INCREASE IN VOLUME				
		3.5 hr.	24 hr.	4 days	6 days	8 days
		%	%	%	%	%
Crude oil:						
Pennsylvania	D-1	17.6	21.7	20.7	20.7	20.7
	R-1	68.4	110.0	261	Disintegrated	
Midcontinent	D-1	26.2	52.7	70	74.2	75.6
	R-1	64.7	130	214	Disintegrated	
Gulf coast	D-1	25	59.2	91	101	102.5
	R-1	58.3	151	342	478	Disintegrated
Spindle oil:						
From Pa. crude	D-1	8.5	20.4	20.4	22.6	22.6
	R-1	45.2	96.0		Disintegrated	
From Midcontinent crude	D-1	15.1	36.4	44.3	49.2	49.2
	R-1	46.0	112.0	349.0	Disintegrated	
From Coastal crude	D-1	28.4	63.7	78.0	86.0	98.5
	R-1	54.4	127.2	410.0	Disintegrated	
Motor oil:						
Essolube	D-1	0.5	3 7	8.4	9.9	9.9
	R-1	18.4	56.8	107.7	131.3	156.8
Sun No. 30	D-1	9.6	26.2	39.1	41.5	44.7
	R-1	32.3	90.4	199.3	260.0	328.0
Atlantic No. 30	D-1	1.3	6.2	10.7	12.3	13.3
	R-1	20.2	53.0	90.3	116.2	140.3
Petrolatum	D-1	2.2	8.9	15.4	17.6	17.6
	R-1	24.3	63.5	114.2	149.2	178.3

[a] All cures, 45 minutes at 287° F (141.7° C.).

EFFECT OF VARIOUS COMPOUNDING INGREDIENTS

Most DuPrene compounds contain small amounts of zinc

oxide, magnesia, and rosin which play an essential part in the vulcanization of DuPrene. The following table shows the formulas for four DuPrene compounds, one of which (842) contains only these vulcanizing ingredients and a plasticizer:

	Compound			
	842	818	820	881
DuPrene type D	100	100	100	100
Zinc oxide	10	10	10	10
Light calcined magnesia	10	10	10	10
Medium process oil	5	5	5	5
Wood rosin	5	5	5	5
Glue	.	10	10	40
Sulfur	.	.	1	1
Soft whiting	.	.	.	110
Brown factice	.	.	.	20
Cottonseed oil	.	.	.	10

Compound 818 is designed to show the effect of adding a small percentage of glue. Compound 820 was run to show the effect of sulfur in addition to glue, and 881 is a commercial stock containing a high percentage of glue and other diluents as well. These compounds were all mold-cured 60 minutes at 287° F. and immersed for 2 weeks in various solvents, in water at room temperature, and in water that was kept boiling continuously by blowing steam through it. The percentage increase in volume is shown in Table VI.

The most important conclusion is that glue, either alone or in combination with sulfur, has a relatively slight effect on the resistance to kerosene, but a much greater effect on the resistance to benzene and carbon tetrachloride. The commercial compound 881, which contains a fairly high percentage of fillers is, as might be expected, considerably better than any of the others in its resistance to organic solvents but absorbs a great deal more water. The effect of glue on absorption is especially pronounced in the boiling water test.

Table VI. Effect of Solvents on DuPrene Compounded with Various Ingredients

Solvent	Volume Increase of Compound[a]			
	842	818	820	881
	%	%	%	%
Benzene	378	313	230	171
Carbon tetrachloride	363	301	224	171
Kerosene	47.7	41.2	39.2	18.3
Water (68° F. or 20° C.)	7.7	8.5	7.9	22.7
Water (212° F. or 100° C.)	28.8	108	130	243

[a] All cures, 60 minutes at 287° F. (141.7° C.).

Channel carbon black increases the oil resistance of DuPrene compounds more than any other pigment, comparisons being made on equal volume loading. The same is true of rubber compounds. However, carbon black has a greater stiffening effect than any other pigment, and, since the hardness of an oil-resistant stock is usually strictly limited by the conditions of service, it is not feasible to use carbon black in as large proportions as other pigments. The semi-reënforcing blacks, such as Gastex, P-33, and Fumonex, can be used in much larger proportions and are therefore generally preferred to channel carbon black. Nonreënforcing fillers, such as whiting, can be used in even larger proportions although they

produce compounds having poorer physical properties than the semi-reënforcing blacks. Clay is not an entirely satisfactory filler because DuPrene compounds containing it have an excessively high permanent set. The effect of the use of other pigments, including barytes, asbestine, zinc oxide, and blanc fixe, have also been studied. Space does not permit presentation of detailed results of these tests, but it suffices to state that no advantage is found by using any pigments other than whiting, glue, and the various grades of carbon black.

Glue is a particularly desirable ingredient for stocks that must resist benzene or other aromatic hydrocarbons. It is desirable in any heavily loaded stock because it is molten at mixing, calendering, and tubing temperatures, and consequently makes more readily workable stocks than other reenforcing pigments.

The use of channel carbon black seems to be desirable only in case service conditions require an oil-resisting stock having also a high abrasion resistance. The semi-reënforcing blacks mentioned above should be used when an oil-resistant stock of moderately high tensile strength and abrasion resistance is required. Whiting should be used as the principal filler when the conditions of service are such as not to require a compound having high tensile strength or abrasion resistance, but merely the best possible oil resistance at the lowest possible cost. The soft blacks, such as Thermax, are but little better than whiting, and it seems that the results with this type of black can be obtained more cheaply with a combination of whiting and one of the semi-reënforcing blacks.

The following formula illustrates the effect of using a high proportion of P-33 carbon black:

DuPrene type D	100.0	Light calcined magnesia	10.0
Wood rosin	5.0	Zinc oxide	5.0
Medium process oil	4.0	P-33 black	114.0
Pine tar	2.0		

Figure 1 shows the percentage increase in volume of this compound, cured 60 minutes at 287° F., when immersed for 279 days in a number of active swelling media. The time of immersion is plotted on a logarithmic scale. This compound has slightly poorer resistance to oils and solvents than compound D-1. The information given by Figure 1 is of particular value because it shows the effect of prolonged immersion of a DuPrene compound in the solvents. Gasoline and ether had practically no effect after the first day; benzene, carbon tetrachloride, and carbon disulfide had so nearly the same effect that it is impossible to show the differences between them on Figure 1. These solvents, together with turpentine, caused a continuous increase in volume of the DuPrene, although the rate of change after the first week was very slight. Medium process oil, on the other hand, was continuously absorbed by the DuPrene at a very slow rate. This test has now been in progress for more than a year and

the sample in medium process oil is still increasing in volume although the rate of increase becomes continually less.

Effect of Prolonged Immersion

The effect of prolonged immersion of DuPrene compounds in kerosene is illustrated by tests that have been in progress for more than two years on the following compound (No. 841–15):

DuPrene	100.0	Neozone D	0.5
Stearic acid	1.0	Benzidine	0.5
Zinc oxide	10.0		

This stock was mixed in February, 1931. A sample cured 30 minutes at 287° F. was immersed in kerosene at room temperature on the day following curing and has been con-

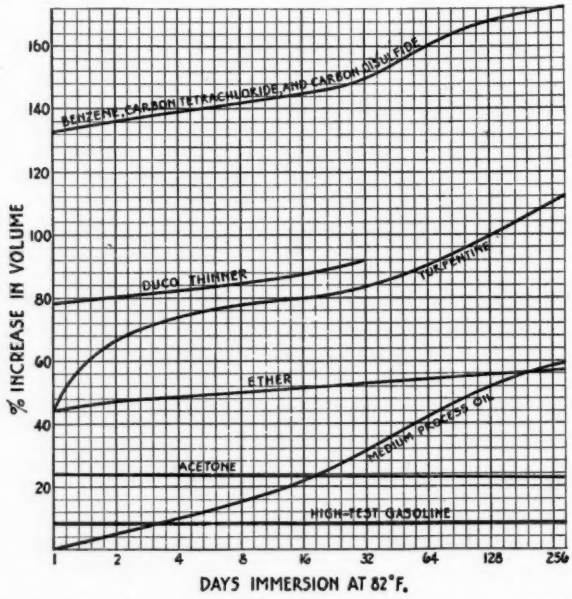

Figure 1. Increase in Volume of P-33 Stock at 82° F. (28° C.)

tinuously kept under kerosene since that time. Table VII shows the results of this test.

The swollen sample was broken for tensile strength after 146 days of immersion when it appeared that the degree of swelling had reached the maximum. There was no change in volume between 146 and 232 days, but thereafter the volume declined quite rapidly until at the end of 730 days the DuPrene was actually swollen less than at the end of the first day. This phenomenon has been noted in a great many DuPrene swelling tests although it is more marked in this case than in any other, presumably because none of the other

TABLE VII. EFFECT OF KEROSENE ON COMPOUND 841–15

PERCENTAGE INCREASE IN VOLUME AFTER IMMERSION FOR:

HOURS					DAYS							
0.5	1	2	4	8	1	3	7	29	146	232	564	730
5.7	8.2	12.0	17.2	25.8	47.5	55.7	60.8	61.0	61.6	60.0	53.0	45.3

	STRESS AT ELONGATION OF:						TENSILE STRENGTH		ELONGATION AT BREAK
	300%		500%		700%				
	Lb./ sq. in.	*(Kg./ sq. cm.)*	*Lb./ sq. in.*	*(Kg./ sq. cm.)*	*Lb./ sq. in.*	*(Kg./ sq. cm.)*	*Lb./ sq. in.*	*(Kg./ sq. cm.)*	%
Original	200	(14.1)	600	(42.2)	1825	(128.3)	2450	(172.2)	750
After 146 days[a]	125	(8.8)	400	(28.1)	..	....	1075	(75.6)	610

[a] Based on thickness after swelling. The physical properties would be considerably higher if the original gage were used for calculating the moduli and tensile strength.

DuPrene swelling tests covers so long a period. At no time during the test has this DuPrene compound shown any tendency toward sloughing off. It is well known that any pure gum rubber compound would completely disintegrate in kerosene in a relatively short period. The value of this test is somewhat decreased by the fact that the type of DuPrene that was available in February, 1931, was far inferior to present day manufacture, as is indicated by the low tensile strength before immersion.

Effect of Acids and Alkalies

The synthetic chemical product on which the whole industrial fabric is most dependent is sulfuric acid. Properly compounded DuPrene is affected hardly at all by cold 50 per cent sulfuric acid. Obviously, acid-soluble pigments such as zinc oxide and whiting should be avoided, and, what is much less obvious, asbestine and clay should not be used in compounds that are to resist sulfuric acid. A compound containing 40 volumes of Dixie clay will swell badly and lose most of its rubber-like characteristics when immersed for only 4 days in boiling 50 per cent sulfuric acid. This is a strenuous test but one that can be met by DuPrene compounds in which carbon black or any of the soft or semi-reënforcing blacks are used as fillers. Results of tests on a typical DuPrene stock before and after boiling for 4 days in 50 per cent sulfuric acid are shown in Table VIII.

Table VIII. Effect of Acids and Alkalies on DuPrene Stock

FORMULA[a]

DuPrene type D	100	Wood rosin	5
Zinc oxide	5	Medium process oil	5
Light calcined magnesia	10	P-33 black	57

PHYSICAL TESTS

Acid or Alkali	Time	Temp.		Tensile Strength		Elongation at Break
	Days	*° F.*	*(° C.)*	*Lb./sq. in.*	*(Kg./sq. cm.)*	%
Original				2725	(191.6)	620
Boiling 50% H_2SO_4	4	314.6	(157)	1150	(80.8)	200
Boiling 50% caustic soda	4	280.4	(138)	2900	(203.9)	380
Boiling 50% caustic soda	8	293	(145)	2700	(189.8)	360
Cold 50% acetic acid	3	68	(20)	2340	(164.5)	471
Cold 50% acetic acid	7	68	(20)	1900	(133.6)	344
Boiling water	10	212	(100)	2750	(193.3)	420

[a] All cures, 60 minutes at 287° F. (141.7° C.).

After this boiling sulfuric acid test the stock is covered with a thin, flaky film of carbonized DuPrene which can be easily scraped off. Cold concentrated sulfuric acid (66° Bé.) has a similar though less severe effect.

Some of the weaker organic acids affect DuPrene to a much greater extent than the strong mineral acids. Acetic acid has a particularly bad effect, being much more harmful to DuPrene than sulfuric acid. Even cold acetic acid causes DuPrene to swell and lose its tensile strength rapidly. However, DuPrene can be made to resist acetic acid moderately well by loading it heavily with clay and channel carbon black. It was stated above that clay is one of the worst pigments

that can be used in a DuPrene stock to resist sulfuric acid, but it is one of the best pigments for stocks that must resist acetic acid. Zinc oxide, whiting, asbestine, and barytes should be avoided, the first two because they react with acetic acid and the last two because compounds containing them swell excessively. A DuPrene compound loaded with 40 volumes of clay will decrease in tensile strength to the extent of approximately 25 per cent after immersion for 7 days in cold 50 per cent acetic acid. Still better results will be obtained if 10 to 20 volumes of a semi-reënforcing black are used in addition to 40 volumes of clay. Weaker acetic acid solutions are much less harmful, such weak solutions as vinegar having very little effect. The effect of acetic acid on a compound containing a semi-reënforcing black is shown in Table VIII.

Caustic soda and other common alkalies have practically no effect on DuPrene. Table VIII shows that boiling for 8 days in 50 per cent caustic soda at 293° F. (145° C.) stiffened the stock somewhat and caused a reduction in the elongation, but the tensile strength was affected hardly at all. The stiffening and reduction in elongation may be largely attributed to the high temperature. There are no special precautions to be observed in compounding DuPrene to resist alkalies except that factice should be avoided.

Conclusion

Since the days of Charles Goodyear there has been among rubber chemists a growing appreciation of the fact that almost every condition of service to which rubber may be subjected requires a different type of compound, if the best possible results are to be obtained. The most valuable lesson to be learned from the investigations reported here is that this is true of DuPrene to an even greater extent than of rubber. It would be easy for one, who had happened to immerse in sulfuric acid a DuPrene compound containing clay, to draw the conclusion that sulfuric acid causes DuPrene to swell and lose all of its strength and rubber-like characteristics; but, when we have all the facts before us, we see that it is the clay, not the DuPrene, that causes the trouble. Likewise, that very common and generally inoffensive rubber-compounding ingredient, barytes, is one of the worst materials that can be used in a DuPrene stock which is subjected in service to acetic acid, but the mere substitution of clay for the barytes produces a stock that is many times more resistant.

The art of DuPrene compounding is still young. In the short time that has elapsed since the invention of DuPrene it has been discovered that DuPrene can be compounded so as to make it more resistant than rubber to practically all chemicals. There is every reason to believe that further experience will teach how to impart even greater oil, solvent, and chemical resistance to this unique synthetic rubber.

[Reprinted from Industrial and Engineering Chemistry, Vol. 26, Pages 33–36, January, 1934.]

Physical Properties of DuPrene Compounds

E. R. BRIDGWATER

E. I. du Pont de Nemours & Company, Wilmington, Del.

Although DuPrene differs chemically from natural rubber, it bears a closer physical resemblance to rubber than any of the previously known synthetic rubbers. It differs from natural rubber in many respects which makes it more suitable for certain purposes and less suitable for others. Its physical properties are susceptible of wide variation depending on the nature and amounts of vulcanizing agents, reënforcing pigments, etc., that are compounded with it, and it fills the need for a rubber-like material having greater resistance to the action of oils and solvents and greater resistance to the deteriorating influences of heat and oxidation than natural rubber.

THERE is perhaps no engineering material that has so wide a range of properties and so great a diversity of uses as vulcanized rubber. By appropriate selection and proportioning of accelerators, antioxidants, reënforcing agents, etc., and by varying conditions of vulcanization one can modify the properties of rubber in almost any desired direction. Service conditions that a few years ago could not be fulfilled with any known type of rubber compound are today being met with modern rubber compounds which may not even involve any new raw materials but merely an artful combination of compounding ingredients that have long been in use.

The rubber chemist has even greater latitude in selecting compounding ingredients for DuPrene than for rubber. Consequently, there is no one ideal DuPrene compound, but rather there are hundreds of DuPrene compounds, each of which represents some chemist's effort to develop the composition best suited to meet a particular set of service conditions.

Likewise, results that we are today unable to obtain with DuPrene we may next year be able to realize, not through improvement in DuPrene itself but through growth in our knowledge of DuPrene compounding.

The purpose of this paper is to compare the physical properties of DuPrene and natural rubber. The most one can do is to compare the properties of certain popular types of DuPrene compounds with similarly compounded rubber stocks. The tests reported in this paper were conducted on two DuPrene compounds, D-10 and D-11, and on two rubber compounds, R-10 and R-11, whose compositions are given in Table I. Compounds D-10 and R-10 are of the pure gum type; that is, they contain only such compounding ingredients as are essential for vulcanization. Compound R-11 is of the type commonly used for tire treads and D-11 is its DuPrene counterpart, both containing 25 volumes of carbon black per 100 volumes of rubber or DuPrene. The two DuPrene compounds each contain 2 per cent of the antioxidant, phenyl-β-naphthylamine. This is perhaps the best antioxidant for DuPrene compounds, and 2 per cent of it is completely soluble in DuPrene, both before and after vulcanization. However, this amount of phenyl-β-naphthylamine is not completely soluble in rubber and, if used in rubber, would bloom to the surface after vulcanization. Therefore, an equal weight of phenyl-α-naphthylamine was used in the rubber compounds since it is an equally efficacious antioxidant for rubber and has the advantage of being more soluble in rubber and, consequently, nonblooming. The DuPrene and the corresponding rubber compounds also differ in other respects. For example, compound D-10 contains rosin and magnesia which are desirable ingredients for DuPrene compounds but are not of particular value in a rubber compound of this type. R-10, on the other hand, contains the accelerator mercaptobenzothiazole, stearic acid, which functions as an activator for the accelerator, and, of course, sulfur.

TABLE I. COMPOSITION OF DUPRENE AND NATURAL RUBBER COMPOUNDS

	D-10	R-10	D-11	R-11
Duprene type D	100.0		100.0	
Smoked sheets		100.0		100.0
Channel carbon black			35.0	45.0
Zinc oxide	10.0	5.0	10.0	5.0
Light-calcined magnesium oxide	10.0		10.0	
Phenyl-β-naphthylamine	2.0		2.0	
Phenyl-α-naphthylamine		2.0		2.0
Wood rosin	5.0		5.0	
Sulfur		3.0	1.0	3.0
Mercaptobenzothiazole		0.5		0.7
Stearic acid		1.0		4.0
Pine tar				2.0
Cottonseed oil			3.0	

CURING RANGE

One of the most desirable properties of a rubber compound is the ability to produce a good vulcanizate over a wide range of time and temperature of vulcanization. This is particularly essential for bulky articles which, on account of the

low heat conductivity of rubber, are vulcanized at a higher temperature on the outside than in the center.

Figure 1 shows the tensile strength and elongation of these four compounds plotted against time of vulcanization at 141° C. The vulcanizing ingredients have been so proportioned that all four compounds reach their optimum cure in approximately 45 minutes. The range of cure of all four appears to be good, bearing in mind that the plateau of the vulcanization curves has been foreshortened by plotting the time of cure on a geometrical scale.

It is noteworthy that the addition of carbon black has but little effect on the maximum tensile strength of DuPrene but nearly doubles the maximum tensile strength of the rubber compound. This is a characteristic behavior of DuPrene as compared with rubber.

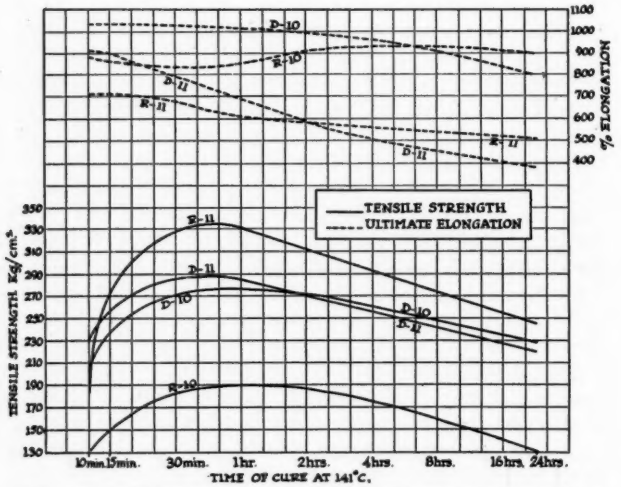

FIGURE 1. TENSILE STRENGTH AND ELONGATION OF COMPOUNDS *vs.* TIME OF CURE AT 141° C.

AGING PROPERTIES

One might conclude from study of Figure 1 that rubber has as broad a range of cure as DuPrene, but the fallacy lies in the fact that compounds R-10 and R-11 have poor tear resistance and aging properties when vulcanized more than 1 hour at this temperature, and when vulcanized for more than 2 hours would be commercially almost useless.

Figure 2 shows tensile-time and elongation-time curves on compounds D-10 and R-10 after aging in the oxygen bomb for 4 days at 70° C. under 300 pounds per square inch (21.1 kg. per sq. cm.) oxygen pressure. It is possible to compound rubber in such a manner as to make it age better than R-10 when badly overcured, but it is quite impossible to produce a rubber compound whose aging properties will be so com-

pletely unaffected by variations in cure as is the DuPrene compound D-10. Neither rubber nor DuPrene is ever cured in such thick masses that the outside of the article gets twenty-four times as much cure as the center, but the aging properties of the long cures are of practical interest to the extent that they indicate the effect on the aging properties of DuPrene or rubber of prolonged exposure to high temperatures in service.

The general experience of this laboratory with compounds of the R-10 type indicates that the 40-minute cure, which is just short of the optimum tensile, has the best aging properties. Consequently, this cure was chosen for further aging tests in the oxygen bomb and in air at 100° C. DuPrene compounds, on the other hand, generally age best when cured to the point of maximum tensile strength, and, as pre-

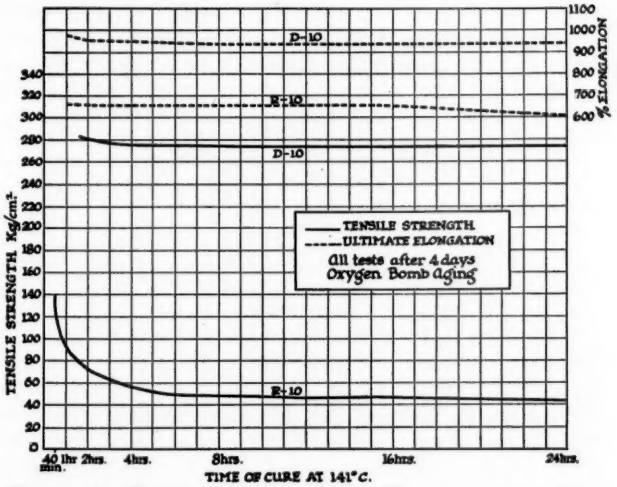

FIGURE 2. TENSILE STRENGTH AND ELONGATION OF COMPOUNDS D-10 AND R-10 *vs.* TIME OF CURE AFTER 4 DAYS IN OXYGEN BOMB

viously shown, prolonging the cure beyond that point causes no deterioration in aging properties. Therefore, compound D-10 (cured 60 minutes) was chosen for prolonged oxygen bomb and 100° oven-aging tests. The results of the oxygen bomb aging tests are shown in Figure 3. The properties of compound D-10 were affected hardly at all by aging for 28 days, whereas R-10 deteriorated badly in 5 days and retained practically no strength at all after aging 4 days. Results of the 100° oven aging tests are shown in Figure 4. In this test the DuPrene compound deteriorated to some extent but at a far slower rate than the rubber compound. Again, it should be pointed out that rubber compounds can be produced to withstand this test better than R-10, but no rubber compound can be produced that will withstand oxygen bomb aging as well as properly compounded DuPrene.

Physical Properties of Vulcanizates

Figure 5 shows stress-strain curves on these four compounds when cured 45 minutes at 141° C. The DuPrene compounds take up load more rapidly during the early stages of extension but more slowly toward the end of the extension. Having observed this difference in a great many comparative tests, one is inclined to regard it as a general characteristic of DuPrene as compared with rubber, although tomorrow a type of compound may be found that will disprove the generalization.

It is even less safe to draw general conclusions as to the comparative abrasion resistance of DuPrene and rubber because so many different types of abrasion are encountered in service and also because temperature, degree of distortion, etc., have such a profound effect. Consequently, there is no laboratory abrasion test that can be relied upon to enable one to predict exactly the difference in abrasion resistances under any given set of service conditions. Table II shows results of abrasion tests on compounds D-11 and R-11 that were run on the du Pont abrasion machine.

Table II. Abrasion Tests

Compound	Cure at 141° C.	Temp. of Test	Abrasion Loss
	Minutes	*° C.*	*Cc./h.p./hour*
R-11	50	28	177
D-11	60	28	184
R-11	50	50	Sticky
D-11	60	50	176

The rubber and DuPrene compounds were cured 50 and 60 minutes, respectively, which seemed to be the cures that would abrade best at 28° C. The DuPrene compound showed slightly greater abrasion loss, but the difference was within experimental error. At 50° C. the rubber compound softened to such an extent that it could not be tested on this machine, although it is undoubtedly a practical compound for a tire tread at an operating temperature of 50° C. In general the abrasion resistance of rubber declines sharply with increasing temperature, but it appears from this test and from observations on other compounds that temperatures up to 50° C., and possibly higher, have but little effect on the abrasion resistance of DuPrene compounds.

A common cause of failure of rubber compounds is flex-cracking. Since this type of deterioration is generally conceded to be intimately associated with oxidation, it is not surprising to find that DuPrene compounds resist flexing many times better than similarly compounded rubber stocks. Compounds D-11 and R-11 were compared on a flexing machine which makes use of a test piece with grooves molded in the outer surface and with a tire fabric reënforcement on the back (Figure 6). The test piece is oscillated under a pulley supporting a 50-pound (22.7-kg.) weight. Under these testing conditions, compound R-11 showed slight nicks

at the base of the design in 8 hours and definite cracks about 1 mm. deep in 14 hours, and was broken through to the fabric base at the end of 24 hours. This is average behavior for a properly compounded tire tread stock under these testing conditions. The test on compound D-11 was continued for 80 hours, at the end of which time no indication of failure was observed. Figure 6 was photographed after 24 hours of running on compound R-11 and 80 hours on D-11.

Oil Resistance

One of the most striking differences between DuPrene and rubber is the greater resistance of DuPrene to the swelling and deteriorating action of oils and solvents that have a notoriously bad effect on rubber. The resistance of rubber to

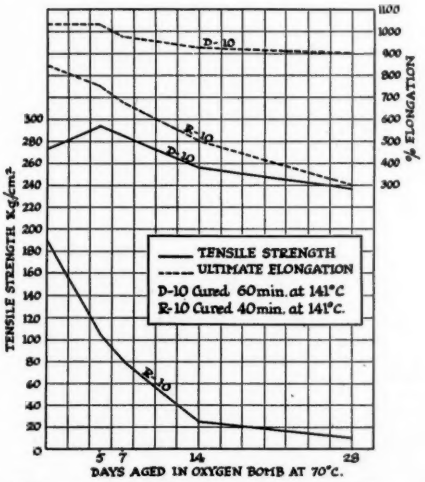

Figure 3. Effect of Oxygen Bomb Aging on Tensile Strength and Elongation of Compounds D-10 and R-10

these deteriorating influences may be greatly improved by loading it heavily with reënforcing pigments, especially certain types of carbon black. Table III shows the formula for a typical oil-resisting rubber stock and for a comparable DuPrene compound containing the same fillers in the same volume relationship. These compounds contain vulcanizing ingredients in such proportions that the DuPrene compound reaches its maximum tensile strength when cured 15 minutes at 141° C., and the rubber compound reaches its maximum tensile strength when cured 5 to 7 minutes at 141° C. It is well known that the oil resistance of rubber is improved by giving it what is technically known as a very tight cure. Consequently, oil immersion tests were run on samples cured 45 minutes at 141° C. The test samples were 2.5 cm. wide,

12.5 cm. long, and 2 mm. thick. These samples were immersed in various swelling media for one week at 28° C. and in some cases at 100° C. Tests were not run at the higher temperature in low-boiling materials such as gasoline, both because they would have little practical value and because of the difficulty and danger of conducting such a test. No test was run in petrolatum at 28° C. because it is a solid at that temperature and consequently it would be difficult to obtain perfect contact of the sample with the swelling medium.

The results of these tests are shown in Table IV. It is clear that the higher the temperature the greater is the difference between the degree of swelling of a rubber compound

TABLE III. FORMULAS OF OIL-RESISTING STOCKS

	R-1	D-1
DuPrene	...	100
Smoked sheets	100	...
Soft whiting (40 vol.)	112	85
Gastex (20 vol.)	38	28.5
Glue (10 vol.)	15	11.5
Zinc oxide	10	10
Light-calcined magnesium oxide	...	10
Cottonseed oil	1	2
Stearic acid	1	..
Wood rosin	...	5
Phenyl-β-naphthylamine	...	2
Phenyl-α-naphthylamine	2	...
Sulfur	6	1.5
Du Pont accelerator 808	1	...

TABLE IV. EFFECT OF IMMERSING COMPOUNDS D-1 AND R-1 IN SWELLING MEDIA FOR ONE WEEK

SWELLING MEDIUM	% INCREASE IN VOLUME AT 28° C.		AT 100° C.	
	D-1	R-1	D-1	R-1
Satd. petroleum derivatives:				
Casing-head gasoline	9	58	...	...
Kerosene	22	78	37	Dissolved
Paraffin-base motor oil[a]	1	11	11	150
Pennsylvania crude oil	10	59	21	Dissolved
Petrolatum	...	..	17	178
Unsatd. petroleum derivatives[c]				
Midcontinent crude oil	20	61	75	Dissolved
Coastal crude oil	18	54	102	Dissolved
Cracked motor gasoline	33	88	...	...
Benzene[b]	174	122	...	...
Carbon tetrachloride[c]	176	172	...	...
Cottonseed oil	2	15	...	...
Linseed oil	4	7	...	...
Turpentine	88	135	...	...
Lard oil	5	12	...	...

[a] Hydrogenated lubricants from unsaturated crudes give similar results.
[b] Toluene, xylene, and solvent naphtha give similar results.
[c] Other chlorinated solvents give similar results.

and of a similar DuPrene compound in any given swelling medium. Rubber can be compounded so as to resist the action of some oils and solvents very satisfactorily at normal temperature, but there is no rubber compound that will not ultimately disintegrate completely when immersed in any petroleum distillate at 100° C.

It has long been known that unsaturated hydrocarbons are somewhat more active swelling agents for rubber than the corresponding saturated hydrocarbons. This is true of DuPrene to a much greater extent than of rubber. It follows that the difference between the swelling of a DuPrene com-

pound and of a similar rubber compound is uniformly greater in saturated than in unsaturated hydrocarbons. In fact, the aromatics, such as benzene which represents the highest possible degree of unsaturation, actually swell DuPrene to a greater extent than rubber at room temperature. It is also true that the difference between compounds D-1 and R-1 is much greater in cottonseed oil which is nondrying than in linseed which is a drying (i. e., unsaturated) oil. Also, turpentine, which has a cyclic structure, swells both DuPrene and rubber quite badly, and the difference between the swelling of DuPrene and of rubber in this medium is relatively slight.

The most important difference between the behavior of DuPrene and rubber in oils and solvents lies not in the degree of swelling but in the toughness and other physical proper-

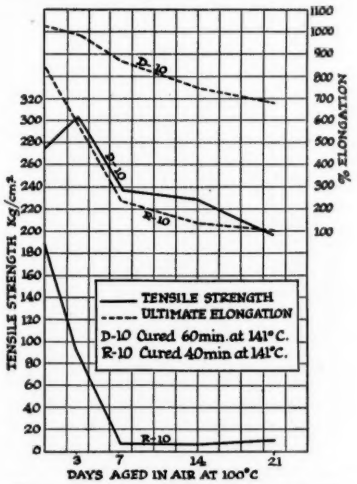

FIGURE 4. EFFECT OF 100° C. OVEN-AGING ON TENSILE STRENGTH AND ELONGATION OF COMPOUNDS D-10 AND R-10

ties after exposure to the swelling agent. Rubber compounds when badly swollen by oils, etc., become quite tender and tend to slough off in tiny particles. DuPrene compounds have no such tendency even though they may be swollen to three or four times their original volume. In fact, a DuPrene compound such as D-1 will retain approximately half of its tensile strength after immersion in kerosene at room temperature for six months, whereas a rubber compound such as R-1 will have only about one-eighth of its original tensile strength after immersion in kerosene for a few days. Tensile strength after immersion in swelling agents is usually calculated with reference to the original cross section before immersion, and the preceding statements are based on that method of calculation.

Other Physical Properties

One of the most important properties of rubber is its hysteresis loss or its mechanical efficiency as a medium for storing and releasing energy. Another important and closely related property is its permanent set which is a measure of the extent to which it fails to return to its original shape after deformation. A detailed study of these properties of DuPrene as compared with rubber is being made and will be reported in a subsequent paper. In general, unpigmented DuPrene stocks containing no sulfur have higher permanent set than sulfur-vulcanized rubber, but the power loss of DuPrene compounds is inclined to be lower than for similarly compounded rubber stocks. Moreover, the addition of sulfur to DuPrene compounds tends to reduce the permanent set or cold flow under compression and to reduce the hysteresis loss. These conclusions are purely tentative and must be accepted with cau-

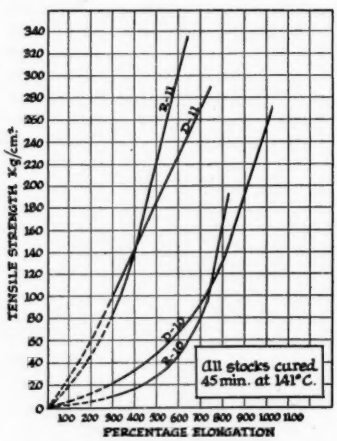

Figure 5. Stress-Strain Curves of Compounds D-10 and R-10

tion because the choice of vulcanizing agents and the conditions of vulcanization appear greatly to affect these properties.

Sun-checking and corona-checking are types of failure of rubber that are believed to be caused by ozone. DuPrene can be made to show these effects under severe conditions but the development of cracks is so slow that under normal conditions DuPrene is not subject to sun-checking and is much less subject to corona-checking than rubber.

DuPrene is less permeable to gases than natural rubber. This is presumably due to the fact that it contains none of the proteins, resins, and other so-called nonrubber constituents of natural rubber which appear to assist in the diffusion of gases.

Although DuPrene can be burned if a sufficiently hot flame is applied to it, it will not support combustion after the source

of heat is removed, whereas natural rubber will. In general, it is chemically more stable than natural rubber, by which is meant that it is more resistant to oxidation and to acids and alkalies and other chemicals that react on rubber.

Rubber cements are made by swelling natural rubber in gasoline and other solvents. DuPrene cements may be prepared in a similar manner, but the range of available solvents is limited to the aromatic hydrocarbons and the chlorinated solvents such as carbon tetrachloride. DuPrene is not soluble in gasoline and other petroleum fractions, even in the unvulcanized form. DuPrene cements are, in general, better adhesives than rubber cements because unvulcanized DuPrene is tougher and less extensible than unvulcanzied rubber and, moreover, the properties of DuPrene are unaffected by dissolving it and removing the solvent by evaporation, whereas rubber appears to undergo some form of deaggregation. In rub-

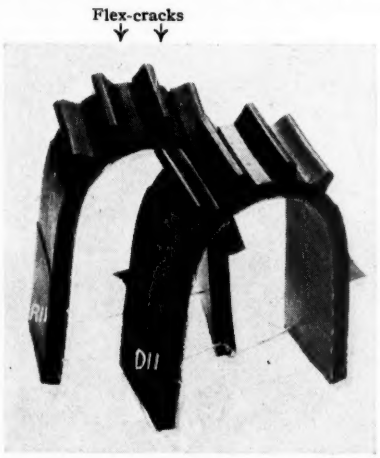

FIGURE 6. FLEX-CRACKING TESTS

ber manufacturers' parlance, DuPrene cements have "shorter legs" than rubber cements.

Since the molecule of chloroprene, of which DuPrene is a polymer, contains a chlorine atom, it is not surprising that DuPrene has a higher specific gravity than natural rubber (DuPrene, 1.21; natural rubber, 0.93).

No attempt has been made in this paper to discuss the art of DuPrene compounding. No evidence is presented to support such statements as the one that DuPrene allows the chemist greater latitude in his choice of compounding ingredients than he has when working with rubber, but a few examples may not be amiss. Sulfur is, of course, essential for the vulcanization of rubber and not essential for the vulcanization of DuPrene although it may in some cases be used to advantage. The vulcanization of natural rubber is retarded by most acids stronger than the higher fatty acids such as stearic.

On the other hand, acidic ingredients such as leather dust may be used to good advantage in DuPrene compounds without affecting the rate of vulcanization. More detailed information concerning the influence of various compounding ingredients may be found elsewhere.[1]

[1] Bridgwater and Krismann, IND. ENG CHEM., **25**, 280 (1933); RUBBER CHEM. & TECH., **6**, 309 (1933).